











# CHEMICAL ABSTRACTS

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## 1—APPARATUS

C. G. DERICK

**Another mercury vapor pump.** L. T. JONES. *J. Optical Soc. Am.* 7, 537-8(1923); cf. *C. A.* 17, 2.—This is similar to other Hg pumps but it is more rugged and has a record of consistent satisfactory performance. A drawing shows the details of construction. It is made of Pyrex glass. D. E. S.

**A platinum substitute suitable for many purposes.** W. A. ROTH. *Verh. Phys. Ges.* 3, 20; *Physik. Ber.* 3, 739(1922).—The silver lining of a Pt-free steel bomb can be well protected against acids by a bromide coating. The coating is only a few thousandths mm. in thickness. After platinizing, a Ag-AgBr plate is a perfect substitute for Pt in detns. of elec. cond., even in solns. contg. thiosulfate or KCN. After passage of a. c. for an hour in half normal  $\text{HNO}_3$  only a few tenths mg. of Ag were lost. For silver coulometers the same substitute is good. A. F. STRAENK

**Optical pyrometer for high current connections.** RETZOW. *Die Wärme* 45, 401; *Chem. Zentr.* 1922, IV, 981.—The pyrometer manufd. by the General Electric Co. (Berlin) compares the brightness of the luminescent body to be measured with that of a filament of an adjustable elec. lamp. By means of adjustable resistance in the circuit the temp. of the luminescent body is detd., with a range of 680–1600° and accuracy of 1%. C. C. DAVIS

**A device for rotating spectrometer crystals.** PAUL KIRKPATRICK. *J. Optical Soc. Am.* 7, 539–41(1923).—This device comprises a ratchet and sprocket wheel on a horizontal shaft. The ratchet is rotated by a pawl actuated by an electromagnet. A light chain passing over the sprocket transmits the rotation to the head of the slow-motion tangent screw of the spectrometer. A means is provided for disengaging the pawl so that the tangent screw may be backed off. A rocker arm which dips into mercury cups is attached to a metronome and furnishes accurately timed contacts for actuating the electromagnet. D. E. S.

**Method for using hydrogen sulfide.** H. REMY. *Chem.-Ztg.* 47, 504–5(1923).—The use of a stoppered flask carrying an inlet and an outlet tube, the latter provided with a stopcock, is recommended in order to give the highest concn. of  $\text{H}_2\text{S}$  in the pipet. flask, intimate contact with soln., economy of materials used, and minimum of discomfort and danger to the operator. The stopcock must be opened occasionally to allow gases other than  $\text{H}_2\text{S}$  (chiefly H) to escape. W. C. E.

**New hardness tester.** ANON. *Iron Steel Can.* 6, 145–8(1923).—A description is given of the Herbert pendulum hardness tester recently invented in England. This instrument gives direct and rapid readings of hardness and can be used for testing the hardness of substances ranging from Pb to sapphire. V. O. HOMERBERG

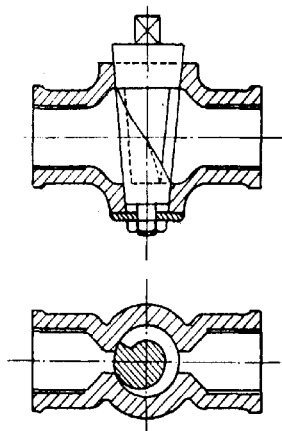
**Steam accumulators.** M. EMANAU. *Chem. Met. Eng.* 29, 149–52(1923); cf. Ginsberg, *C. A.* 17, 2524.—A modern system contains a combustion chamber, an evaporator, a superheater and an accumulator together with the usual auxiliaries used in modern boiler practice, feed water heater, economizer and air preheater. This system reduces the explosion hazard, because the accumulator is not directly heated. The discharge system limits the field of usefulness. The ratio of the initial amt. of water in the accumulator,  $P_0$ , to the amt. remaining at any given time,  $P$ , at a temp.  $t$ , is expressed as  $P_0/P = (606.5 - 0.695t)^{1.44} / (606.5 - 0.695t_0)^{1.44}$ . This equation, plotted, shows that when charged at 25 kg./cm.<sup>2</sup> absolute (223°), the evapn. by expansion can be only  $1/4$  of the wt. of water contained. A second chart shows the wt. of water required in the app. with the source closed to liberate 100 kg. of steam through reduction of temp. Wts. of water required increase rapidly as initial temp. is lowered. A third chart shows the wt. of steam furnished by 1000 kg. water when the accumulator pressure is lowered 1 kg. The speed of discharge is a function of the pressure lowering, vaporization being almost instantaneous. The reverse process of charging (condensation)

is also very rapid but less so than that of discharge. The prime requisites for practical application are rapid and efficient agitation and distribution, good insulation and high capacity. The Halpin, Rateau, Morison, Bell and Ruths accumulators are described.

P. D. V. MANNING

**Acid-proof wooden exhausters in the chemical industry.** H. BÄCKER. *Chem. App.* 10, 103-4(1923).—A brief description of the "Daqua" app., with 2 cuts and a table of capacities and power requirements.

J. H. MOORE



**Gas-pressure regulator.** R. GILMOUR and E. L. COOK. U. S. 1,462,958, July 24.

**Portable acetylene generator.** S. PLUMLEY. U. S. 1,462,623, July 24.

**Mixing chemical reagents with liquids.** W. PATERSON. Brit. 191,762, July 8, 1921. In app. for treating liquids with chem. solns. or powdered reagents the main flow is measured by being passed through a Venturi tube or over a weir, etc., and such measuring means is utilized to proportion the reagent to the main flow of the liquid. The means for measuring the main flow controls the proportioning of the reagent without, however, having any direct connection with the device which adds the reagent.

**Condenser for refrigerating gases.** J. G. HUNTER. U. S. 1,463,468, July 31.

**Apparatus for dehydrating sewage, pulp, etc.** R. A. NORTH. U. S. 1,463,721, July 31.

**Kettle with separate heating and cooling coils in its walls.** J. G. LEHMAN. U. S. reissue 15,865, July 31. See original pat. 1,407,666, C. A. 16, 1520.

**Fine-regulating cock.** E. H. ERIKSEN. Norw. 35,932, Oct. 9, 1922. The edge of the opening for through-flow is helicoidal.

## 2. GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

**Ernst Beckmann.** C. R. PLATZMANN. *Chem.-Zig.* 47, 629(1923).—Obituary.

E. H.

**Dschabir and Geber.** ERNST DARMSHÄDTER. *Chem.-Zig.* 47, 621-2(1923); cf. Lippmann, C. A. 17, 2067.

E. H.

**The cryogenic laboratory of the University of Toronto.** J. C. MCLENNAN. *Nature* 112, 135-9(1923).—App. for the liquefaction of air, of H and of He are described.

E. H.

**The Physical Institute of the University of Leiden from 1904 to 1922.** HENNING. *Naturwissenschaften* 11, 429-30(1923).

C. C. DAVIS

**The history of the teaching of chemistry in Germany.** F. HENRICH. *Chem.-Zig.* 47, 585-7(1923).

E. H.

**Universal and other constants.** ENOCH KARRER. *J. Franklin Inst.* 196, 78-87(1923).—The symbols, formulas, numerical values, and names or definitions of various constns., including those of chem. interest, are presented in tabular form. The relationship of the various constns. to each other is discussed.

JOSEPH S. HEPBURN

**The atomic weight of boron.** ALFRED STOCK and ERNST KUSS. *Z. anorg. allgem. Chem.* 128, 49-75(1923); cf. C. A. 17, 1355.—The at. wt. of B was calcd. from the vol. of H<sub>2</sub> evolved when a weighed quantity of B<sub>2</sub>H<sub>4</sub> is decomposed: B<sub>2</sub>H<sub>4</sub> + 6H<sub>2</sub>O = 2H<sub>3</sub>BO<sub>3</sub> + 6H<sub>2</sub>. The mean value found for the at. wt. was 10.8055 ± 0.0015. The B<sub>2</sub>H<sub>4</sub> was prep'd. by decomp. B<sub>2</sub>H<sub>10</sub> obtained from the treatment of crude magnesium boride with acid. It was purified by repeated fractional distn., and elaborate precautions were taken to prevent its decompn. during the weighing. The at. wt. of Si was det'd. by a similar method by making use of the reaction, SiH<sub>4</sub> + 2NaOH + H<sub>2</sub>O =

$\text{Na}_2\text{SiO}_3 + 4\text{H}_2$ . The mean value found was 28.15, which is considerably lower than the accepted value of 28.3.

**Atomic weight of selenium.** P. BRUYLANTS AND J. DONDEYNE. *Bull. sci. acad. roy. Belg.* [v], **8**, 387–405 (1922).—A previous detn. was made in 1912 (*C. A.* **8**, 1528) and gave the figure 79.18. The weight of a normal l. of  $\text{H}_2\text{Se}$  has been detd. at pressures of 1, 0.6, and 0.3 atm., the 3 values being, resp., 3.6721, 3.65732, and 3.64407 g. The at. wt. of Se is calcd. by making use, in connection with the compressibility values, of the 2 methods recommended by Guye (*C. A.* **13**, 2305), and taking the wt. of a normal l. of O as 1.4289 (Moles and Gonzalez, *C. A.* **10**, 1343). The difference between the new value of the at. wt., 79.37, and that previously obtained is due to 3 causes: (a) The divergence of the compressibility between 0 and 1 atm.  $A_0'$  is, by Guye's method, 0.01083, while the value of  $A_0'$  calcd. from direct measurements of  $p\alpha$  at different pressures and using Berthelot's formula is 0.01302. Guye's method is preferable, because of the high compressibility of  $\text{H}_2\text{Se}$ . (b) The 1912 detns. of compressibility (from measurements of  $p\alpha$ ) give  $A_0'$  0.01191, the d. figures giving  $A_0'$  0.01083. (c) In 1912, the local value of  $g$  was not known; this difficulty was surmounted by actually detg. the wt. of a normal l. of O. These 3 causes of difference all act in the same direction. The above figure (79.37) will therefore be subject to further correction when new data (for compressibility and wt. of normal l. of  $\text{H}_2\text{Se}$ ) are available. A very complete table of vapor pressure measurements from  $t = -78.01^\circ$  ( $p$  82.89 mm.) to  $t = -20.77^\circ$  ( $p$  1799.0 mm.) is given. From these results, the following consts. are obtained:  $b_{268} = 41.2^\circ$ , triple point at  $p$  203.3 mm.,  $t = -65.9^\circ$ ; mol. latent heat of vaporization at  $-41.2^\circ$ ,  $L$  4.76. The b. ps. of  $\text{H}_2\text{Se}$  and  $\text{CS}_2$  give a const.  $T_1/T_2$  ratio between pressures of 230 and 1550 mm. J. C. S.

**Crystal structure of bismuth.** L. W. MCKEEHAN. *J. Franklin Inst.* **195**, 59–66 (1923).—Use of the X-rays of Mo and the powder method indicates a simple rhombohedral space lattice, the rhombohedral axes being mutually inclined at an angle of  $57^\circ 16'$ . The Bi atoms are not uniformly spaced along the trigonal axis. The distances between adjacent atom centers are shown diagrammatically as a result of calcn. J. S. H.

**Molar weight.** OTTO LIGSCHE. *Z. angew. Chem.* **36**, 355–7 (1923).—An appreciative historical resumé of the general subject of molar weight, from the time of Avogadro (1811) to the present, honoring Ernst Beckmann on his 70th birthday (July 4, 1923) for his noteworthy contributions to chemistry. W. C. EBAUGH.

**$\beta$ -Cobaltous iodide.** ERWIN BIRK AND WILHELM BILTZ. *Z. anorg. allgem. Chem.* **128**, 45–8 (1923).—When the ordinary, black, cobaltous iodide (cf. *C. A.* **17**, 2683) is heated to  $300^\circ$ , *in vacuo*, partial decompn. into the elements results and some yellow sublimate is deposited, the compn. of which is represented by the formula  $\text{CoI}_2$ . The d. of this new *allotropic* form,  $\beta$ -cobaltous iodide, is less than that of the ordinary or  $\alpha$ -form. J. A. ALMQUIST.

**Critical quantities.** W. HERZ AND EBERHARD NEUKIRCH. *Z. physik. Chem.* **104**, 433–50 (1923).—Detns. have been made for the first time of the crit. pressure of  $\text{BuOH} = 48.4 \pm 0.5$  atm.,  $\text{C}_6\text{H}_5\text{N} = 60.0 \pm 0.5$  atm.,  $\text{C}_6\text{H}_5\text{OH} = 49.4 \pm 0.5$  atm.,  $p$ -cresol =  $50.8 \pm 0.5$  atm.,  $\text{C}_6\text{H}_5\text{Br} = 61.5 \pm 0.5$  atm.,  $\text{PhNHMe} = 51.3 \pm 0.5$  atm. The following abs. values have been obtained for crit. temp.:  $\text{CHCl}_3 = 535.5^\circ$ ,  $\text{Et}_3\text{NH} = 496.8^\circ$ ,  $\text{Et}_3\text{N} = 535.2^\circ$ ,  $\text{Me}_2\text{CO} = 508.6^\circ$ ,  $\text{Me}_2\text{S} = 502.0^\circ$ , and  $\text{EtBr} = 503.8^\circ$ . These data have been used to test some of the relations published previously by the authors. H. JERMAIN CRRIGHTON.

**Growth of gas bubbles suspended in liquids which are supersaturated with the same gas.** ROBERT FRICKE. *Z. physik. Chem.* **104**, 363–402 (1923).—Formulas are given for the diffusion and hydrodynamic relations of growing gas bubbles rising in liquids which are supersatd. with the gas. These relations have been investigated for  $\text{CO}_2$  by a photographic method. The growth of the bubbles relative to the path traversed divided by the radius is more rapid the larger the bubbles. The velocities of  $\text{CO}_2$  bubbles in water supersatd. with  $\text{CO}_2$  are appreciably greater than in water which is only satd. with the gas. H. JERMAIN CRRIGHTON.

**Determinations of the weight of unit volumes of liquid, solid and semisolid bodies by the aid of a 100-mm. polarization tube.** FERDINAND KRYZ. *Z. Zuckerind. czechoslovak. Rep.* **46**, 472–3; *Chem. Zentr.* **1922**, IV, 653.—If only 10–20 cc. of the material to be examd. is available and there is no 10-cc. pycnometer at hand, a 100-mm. polarization tube calibrated with  $\text{H}_2\text{O}$  may be used instead of the pycnometer. The contents of such a tube amount to less than 10 cc. usually ( $d.$  4.934 and 7.388 cc.). The  $d.$  corresponds with that in the pycnometer up to 3 decimal points, which answers for many technical purposes. In this manner the  $d.$  of oil, varnish, turpentine, crude glycerol and slaked lime paste were detd. C. C. DAVIS.



**Influence of surface tension on melting and freezing.** ERNST RIE. *Z. physik. Chem.* 104, 354-62(1923).—A mathematical paper. The influence of surface tension on the m. p. is investigated thermodynamically, and formulas are deduced for the change in the m. p. A new theory of the structure of glasses is given, and the difference between this and that of Tamann is discussed.

H. JERMAIN CREIGHTON  
**The surface tension of mercury in oxygen.** T. BATUECAS. *Anales soc. españ. fis. quim.* 21, 259-64(1923).—A discussion of the paper abstracted in C. A. 17, 1909.

L. E. GILSON

**Observations and experiments on the phenomenon of the sublimation of some substances.** ATTILIO PURGOTTI. *Ann. scuola agr. Portici* [2], 15, 1-8(1919).—In collections of chemicals it may be observed that vessels contg. sublimable substances have their sides towards the source of light covered with sublimed crystals. The only reference found (in the manual of Dupont and Freundler, Librairie Hachette et Cie, Paris, 1898) attributes this to the effect of heat. A test tube contg. camphor was sealed and completely covered with black paper. Another had only its lower half thus covered. On exposure to light there was no sublimation in the first tube, while crystals accumulated in the upper half of the other. A tube contg.  $\text{SO}_2$  was sealed and completely covered with a thin sheet of brass and placed in a vertical position in a glass beaker filled with  $\text{H}_2\text{O}$  which was kept in rapid motion. The metallic sheath permitted the flow of  $\text{H}_2\text{O}$  between it and the tube since it was not perfectly tight-fitting. A similar tube in the same beaker had only its lower half covered with metal. After 8 days crystals appeared above the edge of the sheet while there was no sublimation at all in the completely covered tube. On replacing the tubes in the beaker, no  $\text{SO}_2$  remained at the bottom of the partly covered tube at the expiration of a month while the covered tube was unchanged. Partly covered tubes were immersed in pure  $\text{H}_2\text{O}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  and indigo solns. After a month those in the  $\text{H}_2\text{O}$  and in the  $\text{K}_2\text{Cr}_2\text{O}_7$  soln. showed abundant sublimation while there was none in that immersed in the indigo. Uncovered tubes were immersed in  $\text{H}_2\text{O}$  and indigo soln. and a third completely covered tube was placed in the  $\text{H}_2\text{O}$ . After several days sublimation was observed in the uncovered tube in the  $\text{H}_2\text{O}$  and none at all in the other 2. P. concludes (1) that temp. differences do not cause the phenomenon, though more rapid sublimation takes place at higher temps.; (2) that sublimation does not occur if the substance is kept in the dark, temp. differences between different parts of the tube being avoided; (3) that under identical conditions of expt. and heat, sublimation takes place into the more illuminated parts of the tube; (4) that yellow (more luminous) rays det. the phenomenon while chem. rays exert no influence. No attempt at a theory for explanation is advanced. ALBERT R. MERZ

**A proposal for the establishment of a new scale of hardness for glass and crystals.** BERNHARD HALLE. *Deut. opt. Wochschr.* 8, 98-100; *Chem. Zentr.* 1922, IV, 101.—After a short summary of older methods and app. a modification of the method of Rosiwal is described. Instead of a definite amt. of abrasive being used until it becomes useless, it is continuously renewed and that used is sepd. out. It is assumed that the hardness is proportional to the loss in wt. under fixed conditions. The abrasive and the necessary liquid (usually  $\text{H}_2\text{O}$ , but olive oil for diamond and  $\text{EtOH}$  or  $\text{C}_6\text{H}_6$  for  $\text{H}_2\text{O}$ -sol. crystals) are enclosed in a 2-section shell and the latter is so rotated that the sample is given a cycloidal motion. The used abrasive is scraped from the lower section of the shell; emery or carborundum is used for soft materials, diamond for hard.

C. C. DAVIS

**Experiments on some capillary phenomena.** ATTILIO PURGOTTI. *Ann. scuola agr. Portici* [2], 15, 1-9(1919).—When a strip of filter paper was dipped into a soln. of chrome aniline black an immediate rapid rise of the liquid took place, followed by a sudden sepn. of the solvent from the solute due to the more rapid rise of the solvent. Two regions were thus formed, one of solvent, the other of solute. The imbibition took place at first with considerable speed but then its rate diminished sensibly. The quantity of solute absorbed at first was not very large but its color became more intense with time, indicating increasing concn. This seemingly strange result was due to continual evapn. of the rising liquid, which prevented further imbibition. On repetition of the expt. under a bell jar in an atm. satd. with moisture there was a greater rise of the solvent and a greater sepn. from the solute. Imbibition stopped at a certain point while the solute continued to diffuse into the moist zone, its color becoming feebler with progressive diminution of concn. Expts. showed that the velocity of imbibition was directly proportional to the width of the strip and inversely proportional to the concn. of the soln. and to the duration of the expt. Sepn. between the solvent and solute was more distinct with increasing concn. of soln. Expts. with anthracene red, blue B. S. I. and other dyes indicate that the capillary rise, besides depending on varying concn. of

the same soln., depends also on the soly. of the different substances in the same solvent, the quantity of solute used in the soln. being the same. Therefore, by mixing different substances in soln. and making use of their different concns. and solubilities it was possible to obtain the sepn. of different dyes from an apparently homogeneous soln. by means of a strip of bibulous paper, the most sol. and least concd. substance always sepg. first. The velocity of diffusion of certain substances was detd. by measuring the distance covered by 2 substances, placed in beakers with a strip of bibulous paper forming a bridge between them, to their point of encounter where they gave rise to a reaction, preferably colored. With equimolecular solns. the path covered in every instance is equal. At the beginning of the imbibition the absorption of liquid occurs with great rapidity but then decreases to assume a uniform rate. The velocity of diffusion is inversely proportional to the concn. of the 2 salts. Microscopic examn., at the moment of formation of the ppt. between the 2 salts ( $\text{FeCl}_3$  and  $\text{K}_4\text{Fe}(\text{CN})_6$ ), shows the formation of a membrane, transversely placed to the strip, which, increasing in size, tends to invade the field occupied by the  $\text{K}_4\text{Fe}(\text{CN})_6$ . "It would seem, then, to be a question of a semipermeable membrane which permits the passage, at least for a certain distance, of the  $\text{FeCl}_3$  but not of the  $\text{K}_4\text{Fe}(\text{CN})_6$ ." A membrane formed from  $\text{CuSO}_4$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  seems to be impermeable to the  $\text{K}_4\text{Fe}(\text{CN})_6$  and therefore the tendency is to enlarge in the direction  $\text{CuSO}_4$ - $\text{K}_4\text{Fe}(\text{CN})_6$ . A membrane formed from  $\text{KI}$  and  $\text{FeCl}_3$  seems to permit the passage of the  $\text{KI}$ ; a membrane from  $\text{KSCN}$  and  $\text{FeCl}_3$  permits the passage of  $\text{KSCN}$ ; a membrane from  $\text{AgNO}_3$  and  $\text{FeCl}_3$  is permeable to the  $\text{FeCl}_3$ . It was sought to obtain 2 different reactions on the same strip by using  $\text{KSCN}$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  in one beaker and  $\text{FeCl}_3$  in the other. The formation of the blue ppt. in the above mentioned direction was first noted and then the formation of the red ppt. in the opposite direction. While the  $\text{FeCl}_3$  passed through the first membrane to increase its length this was impermeable to the  $\text{K}_4\text{Fe}(\text{CN})_6$  but permeable to the  $\text{KSCN}$ , which, proceeding to react with the  $\text{FeCl}_3$ , invaded the field occupied by the latter. With solns. of  $\text{HgCl}_2$  and  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  on one side and of  $\text{KI}$  on the other,  $\text{PbI}_2$  is first formed in the direction towards the acetate. Then, after a time, the  $\text{KI}$  reacts with the  $\text{HgCl}_2$ . This reaction is in the same direction as the first. With  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{CuSO}_4$  on one side and ammonia on the other the membrane permits the passage of ammonia from one side and  $\text{CuSO}_4$  from the other.

ALBERT R. MERZ

A method for the determination of relative sizes of surfaces of adsorbents. I. TRAUBE AND K. NISHIZAWA. *Kolloid-Z.* 32, 392-3(1923).—The wts. of a substance in different degrees of dispersion that will cause an equal lowering in drop number of an equal quantity of caprylic or oleic acid have equal surface areas. B. S. NEUBAUSER

Relation of acidity to carbon dioxide adsorption by certain gels and plant tissues. CORNELIA J. CAREY. *Physiol. Researches* 2, 407-32(1923).—The following exptl. studies were made: (1) The adsorption of  $\text{H}_2\text{O}$  and of solns. of  $\text{HCl}$  and citric acid by gels of agar, gelatin, agar-gelatin, and starch, coconut endosperm free from oil and sol. matter, and dried cotyledons of the white lupine (*Lupinus albus*), Windsor bean (*Vicia faba*) and lima bean (*Phaseolus lunatus*); (2) the occlusion of  $\text{CO}_2$  by gels of agar and gelatin, agar gels contg. glycolic or succinic acid, or malic acid or  $\text{Na}$  stearate, dried cotyledons of the white lupine and Windsor bean, and pieces of the root of the carrot (*Daucus carota*) and tuber of the potato (*Solanum tuberosum*). The usual procedure was to expose the exptl. material to the action of water or an aq. soln. for 24 hrs., ascertain the adsorption of water by gain in wt. and the adsorption of acid by titration of the soln. The exptl. material was then exposed to an atm. of  $\text{CO}_2$  for 24 hrs., and the amt. of  $\text{CO}_2$  adsorbed was detd. by analysis. The amt. of water adsorbed varied with the substance and with the concn. of the acid used. Agar gel swelled in water more than did gelatin, while gelatin swelled in acid solns. more than did agar. The acids were used in concns. between 0.05 and 0.5  $N$ . Gelatin was sensitive to the  $\text{H}$ -ion concn. within these limits, for it showed the greatest water intake in 0.05  $N$   $\text{HCl}$  and 0.5  $N$  citric acid, which have approx. the same  $\text{H}$ -ion concn. Agar-gelatin behaved like gelatin, but less markedly. The other materials did not show this sensitivity to the  $\text{H}$ -ion concn. Increase in the concn. of either  $\text{HCl}$  or citric acid caused an increase in the wt. of acid adsorbed from the soln. by 1 g. of substance.  $\text{HCl}$  had no marked effect on the adsorption of  $\text{CO}_2$  by agar; indications were obtained that the occlusion of  $\text{CO}_2$  decreased as the concn. of  $\text{HCl}$  increased. Agar gel contg.  $\text{Na}$  stearate adsorbed  $\text{CO}_2$  to a greater extent than did pure agar gel, possibly as a result of hydrolytic dissociation of the stearate. Gelatin gel adsorbed more  $\text{CO}_2$  after soaking in water and still more after soaking in  $\text{HCl}$  soln. than did the fresh gel.; this fact is related to the water adsorbed by the gel during soaking. More  $\text{CO}_2$  was adsorbed by samples of plant tissue soaked in water than by similar samples soaked in 0.1  $N$   $\text{HCl}$ . The

results indicate that it is doubtful that increased acidity in the tissues of plants increases the ability of their cells to hold  $\text{CO}_2$ . JOSEPH S. HEPBURN

**Sorption activity of carbon.** J. B. FIRTH. *J. Soc. Chem. Ind.* 42, 242-4T(1923).—The sorption capacities of cane sugar carbonized by (1) heating at low temp., (2) in a vacuum at  $600^\circ$ , and (3) at  $900^\circ$ ; (4) from a sugar soln. mixed with half its wt.  $\text{ZnCl}_2$ , (5) from dry sugar and dry  $\text{ZnCl}_2$ , and (6) from sugar mixed with kieselguhr, were detd. in a 0.1 N soln. in  $\text{CHCl}_3$ . While (1) absorbed only 0.3783 g. I per g. C, (6) absorbed 0.5138 g. The first three were likewise compared as to the rate of decompn. of  $\text{H}_2\text{O}_2$ ; the third was found to be the best. Upbn standing the charcoals decay in activity. It is concluded that the admixed material acts as the spacing agent on which the C is spread "whereby the mol. complexity of the resulting C is considerably reduced" and that the less complex the C mol., the more effective it is as an absorbent. (Cf. C. A. 17, 2071.) BENJAMIN S. NEUHAUSEN

**Adsorption and adhesion pressure: a contribution to the flotation problem.** I. TRAUBE AND K. NISHIZAWA. *Kolloid-Z.* 32, 383-92(1923).—The wetting of, and adsorption by various ores, coal, and gangs of propionic, isovaleric, caproic, and caprylic acids in aq. solns. were studied by the stalagmometer. The formation of a foam layer runs somewhat parallel to the extent of adsorption; there is a direct parallelism in the case of oleic acid. There is no adsorption of solute when the adhesion pressure between the solute and solvent is large but there is complete adsorption when the adhesion pressure is small or the capillary activity is large. When large quantities of absorbent are used, the quantity adsorbed follows Henry's law. BENJAMIN S. NEUHAUSEN

**Hydrous oxides.** V. Hydrous cupric oxide. H. B. WEISER. *J. Phys. Chem.* 27, 601-32(1923); cf. C. A. 17, 1568.—No hydrates of  $\text{CuO}$  are known with certainty. The clear blue gelatinous oxide changes slowly at room temp. through various shades of blue to green, brown and finally black as a consequence of agglomeration of particles, which accompanies the spontaneous loss of water. The blue gelatinous oxide kept at  $0^\circ$  goes over spontaneously to a denser and bluer granular product. Any no. of hydrous oxides can be obtained that vary continuously in compn. from  $\text{CuO} \cdot 20\text{H}_2\text{O}$  to  $\text{CuO} \cdot \text{H}_2\text{O}$ . The gelatinous oxides adsorb ions strongly. If shaken with solns. of neutral salts like  $\text{NaCl}$ , hydrolysis takes place and the soln. becomes distinctly alk. because of stronger adsorption of acid than of base. The adsorption of certain salts slightly accelerates the spontaneous loss of water. Hydrous  $\text{CuO}$  may be heated at  $100^\circ$  without darkening in the presence of very small amts. of  $\text{MnSO}_4$ ,  $\text{CoSO}_4$ ,  $\text{Al}(\text{SO}_4)_3$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ,  $\text{ZnSO}_4$ ,  $\text{CuSO}_4$ ,  $\text{ZnCl}_2$  and  $\text{CuCl}_2$ . This increased stability in the presence of certain salts is not due to the formation of basic salts or to adsorption of the hydrous oxides of their metals. The evidence against the stabilization theory is that hydrous  $\text{CuO}$  adsorbs acids more strongly than bases, that relatively high concns. of colloidal hydrous oxide are not effective and that  $\text{CuSO}_4$  is as effective as  $\text{MnSO}_4$ ,  $\text{Cr}_2(\text{SO}_4)_3$ , etc. The stability of the blue oxide is due to a change in the physical character from the highly gelatinous to the granular form. Only salts of strong acids that hydrolyze appreciably are effective in low concns., since the slight solvent action of the H ion destroys the gelatinous structure and the denser granular modification which forms loses water less readily than the loose voluminous mass. HARRY B. WEISER

**Investigations of ferric hydroxide sol. I. A case of negative osmosis.** JOHS. LINDEMAN. *Kolloid-Z.* 32, 376-83(1923).—The osmotic pressures of several  $\text{Fe}(\text{OH})_3$  sols with and without the addition of  $\text{FeCl}_3$  to the sols were measured against distd.  $\text{H}_2\text{O}$  as well as dil.  $\text{FeCl}_3$  solns. It is concluded that the rate of increase of osmotic pressure is a resultant of the rates of ingress and exit of  $\text{H}_2\text{O}$ . The rate of exit of  $\text{H}_2\text{O}$  is increased by the addition of  $\text{FeCl}_3$  and may even surpass the rate of ingress, which is usually greater; as a result there is a minimum point in the osmotic-pressure curve. The electrolyte content of the sols detd. largely the rate of increase of osmotic pressure with time. (Cf. Biltz, C. A. 4, 1418.) BENJAMIN S. NEUHAUSEN

**Formation of anomalous Liesegang bands.** F. G. TRYHORN AND S. C. BLACKTIN. *Trans. Faraday Soc.* (advance proof) (1923).—Periodic or Liesegang banding of ppt., exhibited when an aq. soln. of an ion is allowed to diffuse into a gel soln. of a pptg. ion, is due to very slow pptn. during which the pptg. ion itself is adsorbed by the ppt. and the medium is cleared of this ion. Diffusion of the entering ion proceeds without further pptn. until this zone is passed, after which another band is formed together with a clear zone. Banding accompanies very slow pptn. only. The cause of low pptn. rates in gels is probably the adsorption of gel by the ions. These adsorption reactions are probably exothermic and are reversed under the influence of supplied external energy, accounting for the increased rate of crystn. observed in the case of three sets of pptg. ions under the influence of light. This increase in rate is such that the pptg. ion is not com-

pletely exhausted from the surrounding medium. A sufficient concn. of this ion remains in the comparatively clear zone to cause slow crystn. and the formation of an additional band. The three cases in which light was found to increase the rate of pptn. also displayed this phenomenon of anomalous banding, but only when exposed to the light. Other sets of ions whose pptn. rates are not noticeably affected by light gave normal banding both in the dark and in the light.

C. R. PARK

**The mechanism of gels. I. The properties of elasticity of several textile threads.** RUDOLF AUERBACH. *Kolloid-Z.* 32, 369-73(1923).—The moduli of elasticity and torsion of woolen and cotton threads were detd. For the torsion measurements A. devised a special modification of Coulomb's method. The results point to a marked anisotropy of the threads; while the elasticity modulus is equal to 100 kg./mm.<sup>2</sup> and thus the threads behave like solids, the torsion modulus is about 0.05 kg./mm.<sup>2</sup> as in gels with a high water content.

BENJAMIN S. NEUBAUSSEN

**The influence of neutral salts on silica gels.** S. GLIXELLI. *Compt. rend.* 176, 1714-6(1923).—When suspended in water, a purified sample of SiO<sub>2</sub> gel was acid. The addn. of neutral salts increased the titratable acidity. In equiv. amts. Na<sub>2</sub>SO<sub>4</sub> had the least effect, followed by NaCl, KCl, and CaCl<sub>2</sub>, resp. This effect is probably due to the adsorption of OH ions by the particles of SiO<sub>2</sub>, because there is a corresponding increase in their negative charges.

WM. STERICKER

**The effect of heat on the precipitate formation in gels.** R. E. LIESegang. *Kolloid-Z.* 32, 263-4(1923).—Diffusion of 20% AgNO<sub>3</sub> into 10% gelatin at about 8° forms AgCl turbidity. At a higher temp. the turbidity disappears, but reappears when the mixt. is brought back to the first temp. Gelatin contg. traces of Na<sub>2</sub>SO<sub>4</sub> shows the same effect.

A. MUTSCHER

**Turbidity of barium sulfate suspensions in transmitted and reflected light.** A. W. OWG. *Kolloid-Z.* 32, 73-7(1923).—BaSO<sub>4</sub> prepd. in glycerol-water and glycerol-alc. mixts. and examd. with the Kleinmann nephelometer were found not to give for particles of the same size, the same readings if prepd. in different dispersion mediums. Different cryst. forms and refractive indexes are the cause, each mixt. giving a different characteristic curve. Turbidity in these mixts. is a max. around 200μ in reflected light. In transmitted light there is regular increase with a max. probably over 1000μ.

A. MUTSCHER

**Diminishing the attack of alkali solutions on aluminium by the addition of water glass.** RÖHRIG. *Chem.-Ztg.* 47, 528-9(1923).—In extending studies reported by Seligman and Williams (*C. A.* 16, 3803) that a soln. contg. 5% of soda and only 0.05% water glass, at a temp. of 75°, was without noticeable effect upon Al, because of the formation of a layer of Al silicate over it, it was found that solns. contg. 0.5 g. NaOH and 0.5 g. water glass per l. would not attack Al even when boiled with it for 15 days, but with 1.0 g. or more of NaOH per liter the evolution of gas began in about 10 hrs., with corresponding soln. of Al; solns. of Na<sub>2</sub>CO<sub>3</sub> in all concns. were without effect upon Al if even 0.05% of water glass were present. Similarly solns. of Na<sub>2</sub>S failed to attack Al in the presence of water glass. The protective coating of Al silicate was stable in the presence of NaOH soln. contg. 0.5 g. per l., but not when it contained 1.5 g. per l. Upon heating, the coating lost but little of its protective power against soda solns., when cold, but was not effective against hot solns. of the same concns. The addition of 0.06% water glass to solns. in app. used in cotton dyeing processes protected it effectively. Al alloys behave like the pure metal in alkali solns. to which water glass is added.

W. C. EBACCHI

**Chemical behavior of disperse substances. Disperse aluminium oxide. II.** V. KOHLSCHÜTTER AND NELLY NEUBENSWANDER. *Z. Elektrochem.* 29, 246-50(1923); cf. *C. A.* 14, 242.—The chem. behavior of disperse Al(OH)<sub>3</sub>, obtained by topochem. decompn. of cryst. salts, has been studied both qual. and quant. with reference to the dependence on the conditions of its formation. Sol formation precedes dissoln. of the hydroxide in concd. HCl, but not in NaOH. On the other hand, sol formation takes place both with acids and bases in the case of Al<sub>2</sub>O<sub>3</sub>. The sol formation, which was followed both by cond. measurements and analytically, was found to be accompanied by chem. decompn.

H. JERMAIN CREIGHTON

**Theory of the ionogen union as basis for the ionization theory.** A. HANTZSCH. *Z. Elektrochem.* 29, 221-46(1923).—The results of expts. on the nature of non-ionized acids are discussed. Carboxylic acids exist in 2 forms: "true acids" which are almost identical optically with their salts and ions, and "pseudo acids" which are optically similar to their esters. In addition to these and acting as a connecting link between them are the so-called "equilibrium acids," which markedly alter the nature of the non-dissocd. solvent. These conclusions are based on the following: (1) Both substitutions

between atoms or at. groups which are practically transparent in the ultra-violet (e. g., H, Na, CH<sub>3</sub>) and additions of transparent substances (e. g., H<sub>2</sub>O, alc., Et<sub>2</sub>O, NH<sub>3</sub>) to substances which absorb in the ultra-violet, change their light absorption either not at all or very slightly. (2) The dissoc. in aq. soln., which is brought about chemically through the addition of H<sub>2</sub>O, is an optically indifferent process in the ultra-violet and visible spectral regions; or: undissocd. electrolytes are optically identical with their ions in aq. soln. The color, which according to the classical ionization theory is ascribed to the ions, is due also to the undissocd. substance. All intrinsic variations in the light absorption due to so-called chem. changes are brought about by constitutive changes due to substitution or addition processes. The strength of non-dissocd. acids has been detd. by (1) measurements of the velocity of inversion of C<sub>12</sub>H<sub>17</sub>O<sub>11</sub>, (2) measurements of the velocity of decompn. of diazoacetic ester and (3) by means of indicators. According to the results of these measurements homogeneous HCO<sub>2</sub>H consists of 95% pseudo-acid and 5% true acid; homogeneous CH<sub>3</sub>CO<sub>2</sub>H >99.9% pseudo-acid and 0.0060% true acid; homogeneous C<sub>2</sub>H<sub>3</sub>CO<sub>2</sub>H >99.9% pseudo-acid and 0.0013% true acid; homogeneous C<sub>3</sub>H<sub>7</sub>CO<sub>2</sub>H >99.9% pseudo-acid and 0.0010% true acid. These ratios are not altered appreciably between 0° and 50°. The results of these measurements show that indicators do not primarily show the concn. of the H<sup>+</sup> ions, but (approx.) the concn. of the ionogen-bound H. The change of the degree of acidity by certain solvents has been studied. The bearing of pseudo HNO<sub>3</sub> on the chem. theory of acids, and the non-existence of many true acids and the majority of acid salts in the solid state are discussed. The following topics are treated briefly: soly. relations of true and pseudo acids; hydrogen halides; generalization of the oxonium theory; the theory of true and pseudo-salts; the cause of the optical effects in the transitions between electrolytes and non-electrolytes; the tendency of salt-formation as a measure of the strength of acids; characteristics of ionogen H. The chem. inactivating influence of Et<sub>2</sub>O is discussed and explained. It is pointed out that in Et<sub>2</sub>O solns. of acids and pseudo acids there exist: (1) true oxonium salts, e. g., ClO<sub>4</sub>[HO(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>], which are similar to true acids but which react more weakly; (2) pseudo oxonium salts, e. g., O<sub>2</sub>N.OH(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, which like the pseudo acids are chem. indifferent; (3) equil. between both series of salts. Conclusions drawn from the acidity of non-dissocd. acids and from the existence of pseudo acids are presented, and the bearing of these conclusions on the modification of the ionization theory by the theory of ionogen union is discussed. In conclusion, acids and pseudo acids are characterized as follows: True acids are heteropolar H compds. contg. ionogen-bound, active H atoms which are replaceable by strongly positive metals or complex cations, resulting in the direct formation of salts, which is not accompanied by constitutive change or appreciable optical change. Their true strength is detd. by the magnitude of their tendency to form salts in the non-dissocd. state. These acids in aq. soln. unite with H<sub>2</sub>O to form hydroxonium salts, which on account of their instability react like the free acids but more weakly than these. Pseudo acids are homopolar H compds. contg. inactive H atoms. In O acids the H atoms are united to the O atoms as hydroxyl. By the addition of H<sub>2</sub>O these acids are partially or wholly converted into hydroxonium ions, and in consequence of the constitutive and optical change in the acid radical they react like true acids.

H. JERMAIN CREIGHTON

Second dissociation constant of sulfoacetic and  $\alpha$ -sulfopropionic acids. H. J. BACKER. *Proc. Acad. Sci. Amsterdam* 26, 83-7(1923); cf. *C. A.* 17, 1180.—In the preceding paper the 2nd dissoc. const. was calcd. from measurements of the cond. of the acid salts. In the present paper these consts. have been obtained colorimetrically from the  $p_H$  of the acid salt and also from the  $p_H$  of mixts. of neutral and acid salts. The mean result of the 3 detns. are: sulfoacetic,  $k_2$  7.4, 9.7,  $7.2 \times 10^{-4}$ ; sulfopropionic, 4.8, 6.0,  $4.2 \times 10^{-4}$ . It is seen that the order of magnitude is the same for the const. detd. in various ways.

C. J. WEST

The distribution of the solvent among the dissolved substances. ANTOINE DOROSHEVSKII. *Bull. soc. chim.* 33, 550-9(1923); cf. *C. A.* 8, 288, 2515, 3143; 9, 2173; 10, 2822; 11, 2985.—A posthumous summary of D.'s method for computing the phys. properties of a soln. contg. two solutes and some examples of its application.

JACOB CORNOG

Graphic interpretation of the law of A. Doroshevskii. W. SWIENTOSLAWSKI. *Bull. soc. chim.* 33, 560-1(1923); cf. preceding abstract.—According to the law of D., a phys. property of a liquid mixt. consisting of 2 substances A and B dissolved in a solvent C can be calcd. by  $Z = [Z_A n_1/(n_1 + n_2)] + [Z_B n_2/(n_1 + n_2)]$ . A simple graphic expression is obtained by plotting  $n_1/(n_1 + n_2)$  as abscissae and the values for Z<sub>A</sub> and Z<sub>B</sub> on 2 vertical lines detd. by the points  $n_1/(n_1 + n_2) = 0$  and  $n_2/(n_1 + n_2) = 1$ , i. e.,

at 0% and 100% of *A* in the mixt.  $Z_A = (m_1 + NM)z_A$  and  $Z_B = (m_2 + NM)z_B$ , where  $m_1$ ,  $m_2$  and  $M$  are the mol. wts. of *A*, *B*, and the solvent resp. and  $z_A$  and  $z_B$  are values for the phys. property calcd. for 1 g. of soln. A straight line joining  $Z_A$  and  $Z_B$  represents the variation of the physical property for any mixt. providing the total no. of solvent mols. is const. and the sum of the mols. of *A* and *B*, or  $n_1 + n_2 = 1$ .

J. CORNOU

**Velocity of chemical reactions.** J. A. CHRISTIANSEN AND H. A. KRAMERS. *Z. physik. Chem.* **104**, 451–71 (1923); cf. *C. A.* **17**, 916.—A mathematical paper which deals with theories of unimol. reactions, and the occurrence of unimol. reactions. A no. of unimol. reactions recently studied are tabulated.

H. JERMAIN CREIGHTON

**Rate of reaction of oxygen, nitric oxide and nitrous oxide on metals.** E. SCHROEDER AND G. TAMMANN. *Z. anorg. allgem. Chem.* **128**, 179–206 (1923).—The rate of attack on Fe and Ni by  $O_2$  is independent of the pressure of  $O_2$  within wide limits. Even at low pressures, which for Fe are especially low, the initial rate of film formation falls off rapidly with diminishing  $O_2$ -pressure. Plotting the initial rate (at const. temp.) against the pressure yields a curve similar to the absorption isotherm of gases in C. It is to be assumed that on the oxide film there is a layer of adsorbed  $O_2$ . The oxidation of Cu is especially abnormal, for at low pressures more Cu oxidizes than at high pressures. Although there is a greater initial rate of oxide film formation at the higher pressures, yet there is greater permeability of film at the lower pressures, so that in time the film is thicker. At 760 mm. the effect of  $O_2$  and NO is the same at the same temp. and greater than the effect of  $N_2O$ . For Ni in NO and  $N_2O$  there is initially a difficultly permeable film which at a thickness giving a color equal to a 280  $\mu$  air film, changes to a permeable one. After the formation of this permeable film the behavior of Ni in NO and  $N_2O$  is similar to that of  $O_2$  and of  $N_2O_2$  mixts. at a partial pressure higher than 150 mm.

JAMES M. BELL

**Procedure for the study of the speed of formation of precipitates.** R. G. BOUSSSE. *Compt. rend.* **176**, 93–5 (1923).—Studies were made of the relationship between the speed of formation of ppts. from supersatd. solns. and such factors as concn., temp., viscosity, etc. The app. used was that of Jolibois (*C. A.* **14**, 607). The solns. were brought together by admitting them to the 2 arms of a Y tube and after traversing various heights were led into a large vol. of satd. soln. The time in sec. was noted and plotted against the percentage of the wt. of substance pptd. A typical curve is given for the case of  $CaC_2O_4$  formed by admixing a soln. of  $Ca(NO_3)_2$  and  $H_2C_2O_4$ .

D. T. EWING

**Influence of intensive drying on internal conversion.** I. A. SMITS. *Proc. Acad. Sci. Amsterdam* **26**, 266–9 (1923).—The inactivation of certain substances such as HCl and  $NH_3$  upon intensive drying is due to the existence of 2 types of mols. The drying process shifts the equil. between these two types in the direction of formation of the inactive mol. No exptl. data are given.

C. R. PARK

**The system sulfur trioxide.** I. A. SMITS. *Proc. Acad. Sci. Amsterdam* **26**, 270–3 (1923).—Introduction of a series of articles. No data are given.

C. R. PARK

**Water vapor equilibrium above iron, tungsten and their oxides.** LOTHAR WÖHLER AND R. GÜNTHER. *Z. Elektrochem.* **29**, 276–85 (1923).—The Fe- $H_2O$  equil. above the phases Fe/FeO, FeO/Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub> have been detd. both by oxidation and reduction. Below 570° the results indicate the identity of the  $K_2$  values for Fe<sub>3</sub>O<sub>4</sub>/FeO with the  $K_1$  values for FeO/Fe, thus confirming the latest measurements of van Groningen and Chaudron. The quadruple point of the system Fe/FeO/Fe<sub>3</sub>O<sub>4</sub>/O<sub>2</sub>, below which FeO is unstable, decomposing into Fe and Fe<sub>3</sub>O<sub>4</sub>, lies accordingly at 570°. From the logarithmic representation of the detd.  $K$  values, a general equation of the reaction isochore, of the form  $\log K = -(Q/4.571T) + C$ , has been deduced for the measurements of the 3 systems. By combining this equation with that for the dissoc. of  $H_2O$  vapor, a general equation has been derived for the dissoc. equil. of the oxides of Fe, and the  $O_2$  pressure has been calcd. for several temps. With help of the formula  $E = (0.0002/4) T \log (p_1/p_2)$  the e. m. f.s. of the FeO/Fe and the Fe<sub>3</sub>O<sub>4</sub>/FeO oxidation chains have been calcd. At temps. below 560° it is not possible to reduce Fe<sub>3</sub>O<sub>4</sub> without going directly to metallic Fe. A method has been worked out for the prepn. of pure WO<sub>3</sub> and W<sub>2</sub>O<sub>5</sub>. The oxides prepd. in this way were employed to det. the const. of the W- $H_2O$  equil. above the phases WO<sub>3</sub>/W<sub>2</sub>O<sub>5</sub>, W<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>, and WO<sub>3</sub>/W. The equation of the reaction isochore has been derived from the exptl. results by graphic interpolation. General equations have also been derived for the dissoc. equil. of the oxides of W, and the  $O_2$  pressures calcd. at a no. of temps.

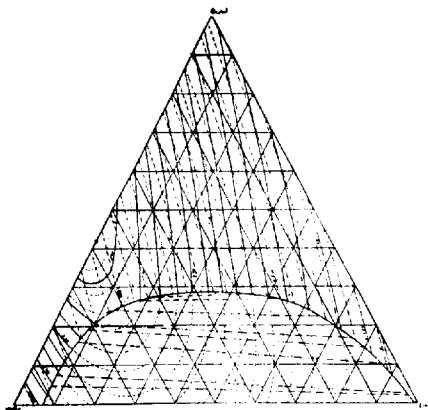
H. JERMAIN CREIGHTON

**Ternary system antipyrine-caffeine-water. Migrainin.** ROBERT KREMANN AND EMMERICH JANETZKY. *Monatsh.* **44**, 49–63 (1923).—Migrainin is a mixt. of about 90 parts antipyrine (I), 9 parts of caffeine (II) and 1 part citric acid with 8 parts H<sub>2</sub>O.

In order to det. the role of the citric acid, a phase-rule study of I, II and  $H_2O$  was undertaken. I and II form a simple eutectic mixt. at  $103^\circ$  with 13% I. The eutectic of  $H_2O$  (ice) and I lies at  $-3.3^\circ$  and 37.5% I. II and  $H_2O$  (ice) form a eutectic at  $-0.4^\circ$  and about 4% II hydrate. There is a sharp break in the soly. curve at  $61^\circ$  (31%), which may be the transformation point of the hydrate into the anhydrous form. Curves are also shown for mixts. of I and II with  $H_2O$ . Finally all the curves are combined into a ternary diagram, and the various fields are discussed.

**Calculation of mixtures graphically.** F. FETTERWEIS. *Chem.-Ztg.* 47, 465(1923).—“Gibbs's triangle” is employed ordinarily to represent the proportions of components in a 3-component system, but this can be simplified to a 2 coordinate system if the proportions of 2 of the components are known, and the 3rd is then computed as the difference between the sum of the above 2 and 100%. Illustrations are given for mixts. contg. known % of 2, 3, or 4 components.

**Ternary system ethyl alcohol-ethyl ether-water.** MASUTARO KONO. *J. Chem. Soc. Japan* 44, 406-19(1923).—Abs. alc. was prepd. over anhyd.  $CuSO_4$  and its purity checked with sp. gr.;  $Et_2O$  was purified with Na (sp. gr. 0.7189), and  $H_2O$  was several times redistd.



--- iso-density points  
 --- iso-viscosity points  
 • max. viscosity point.

of the liquidus curve intersecting at a eutectic point. A solid soln. is formed at the FeS end of the series with limit of soly. at 92.5% FeS and at the  $Cu_2S$  end with limit of soly. at 50%  $Cu_2S$ . The eutectic point is at 68% FeS. The f. p. of FeS is  $1163^\circ$ , of  $Cu_2S$   $1128^\circ$ , of the eutectic  $995^\circ$ . No compd. is formed. A transformation occurs in the solid state at  $950^\circ$ ; this is probably due to a dimorphic change in the crystal habit of  $Cu_2S$ . In the range 15 to 45%, FeS, if a melt is heated considerably above the m. p., metallic Cu separates on cooling accompanied by expansion of the charge sometimes sufficient to break the crucible. This is due to loss of S by distn., with reaction of the liberated Fe on  $Cu_2S$ . A mat of 32% Cu (60% FeS) showed gradual loss of S by distn. when held at  $1100^\circ$ . Photomicrographs are given and the exptl. procedure is described.

A. BURTS

**The molecular state of nitrogen peroxide in solution at low temperatures.** PAUL PASCAL. *Bull. soc. chim.* 33, 539-48(1923).—Cryoscopic methods were used to det. the mol. wt. of  $NO_2$ . Since  $NO_2$  formed mixed crystals with most solvents, the mol. wt. was calcd. by the equation  $\Delta\theta = K(C - C')/M$ , where  $C$  and  $C'$  are resp. the concn. of liquid and of mixed crystals for the substance having a mol. wt.  $M$ . The highest value found was 92, corresponding to  $N_2O_4$ . Eutectic points for the different solvents were: with 23.5%  $CHBr_3$ , at  $-13.5^\circ$ ; 91.85%  $CCl_4$ ,  $-49^\circ$ ; 86%  $C_6H_6Br$ ,  $-42.5^\circ$ ; 91.5%  $CHCl_3$ ,  $-68^\circ$ ; 92% chloropicrin,  $-79.5^\circ$ ; 90%  $CH_3I$ ,  $69.5^\circ$ ; 29.4% picric acid,  $-13.5^\circ$ ; 20% trinitrotoluene,  $-17^\circ$ . Camphor gave 3 eutectic points: with 39.5%

C. J. WAGR  
 W. C. EBAUGH  
 The sp. gr. was detd. by pycnometer and the viscosity by the Ostwald method at  $15^\circ \pm 0.1^\circ$ . The less viscous portion with alc. ether was detd. by Nakano's viscometer (*C. A.* 16, 2987). The result of various points of the system detd. by viscosity and density at  $25^\circ$  are plotted in the diagram scaled at each 20 intervals of viscosity and each 0.01 of sp. gr. According to this diagram, the max. viscosity of 301 is found for a mixt. of alc. (42%) and  $H_2O$ . S. T.

**The equilibrium diagram of the system  $Cu_2S$ -FeS.** C. B. CARPENTER AND C. R. HAYWARD. *Eng. Mining J.-Press* 115, 1055-61(1923).—The diagram is of the usual type in which the 2 components of the system are completely sol. in each other when liquid, but only partly so when solid, the 2 branches

camphor at  $-60^\circ$ ; 65.5%, at  $-55.5^\circ$ ; and 74%, at  $-46.5^\circ$ . Two compds. were established which were easily dissociated at their fusion point and had the compns. resp.  $5\text{N}_2\text{O}_4 \cdot 4\text{C}_{10}\text{H}_{16}\text{O}$  at  $-60^\circ$  and  $2\text{N}_2\text{O}_4 \cdot 3\text{C}_{10}\text{H}_{16}\text{O}$  at  $-46.5^\circ$ . H. M. McLAUGHLIN

**Change in position of acid groups in solid phases.** II. J. A. HEDVALL AND JOSEF HUBERGER. *Z. anorg. allgem. Chem.* **128**, 1-14 (1923).—The study of reactions between carbonates and oxides (cf. *C. A.* **16**, 4117) is extended to *sulfate-oxide* systems. When one of the oxides BaO, SrO, CaO, or MgO is heated with the sulfate of a less positive metal, the  $\text{SO}_4$  group is transferred to the more basic oxide at a temp. far below the dissociation temp. of the sulfate. The temp. required increases with decreasing basicity of the free oxide, and with increasing basicity of the oxide bound in the sulfate. The heat effect, as judged by the rate of increase of the temp. with time, is larger the greater the difference in basicity of the free and the bound oxide. The sulfates of Sr, Ca, Mg, Zn, Cu, and Fe were used with the free oxides named above. J. A. A.

**The determination of double salts in solution by the ebullioscopic method.** F. HOURION AND E. ROUYER. *Compt. rend.* **176**, 1708-10 (1923); cf. *C. A.* **17**, 1181. Ebullioscopic measurements were made and the compn. of various double salts computed by the rule of mixts. It was found that  $\text{CdCl}_2$  forms double salts with KCl,  $\text{NH}_4\text{Cl}$  and NaCl characterized by the type  $2\text{CdCl}_2 \cdot 3\text{MCl}$ . L. T. FAIRHALL

**The use of dyes as temperature indicators.** P. A. KOBER. *Ind. Eng. Chem.* **15**, 837-8 (1923).—The disappearance of or change in color of certain dyes indicates that the part to which the color has been applied has been exposed to a definite temp. for a definite length of time, i. e., it has received a definite amt. of heat. Green, blue and red are the most suitable colors to select. Examples are given and applications are suggested. E. G. R. ARDAGH

**The measurement of temperature in rubber and insulating materials by means of thermocouples.** E. B. SPERAR AND J. F. PURDY. *Ind. Eng. Chem.* **15**, 842-5 (1923). The temps. in fires, etc., indicated by thermocouple employing the methods hitherto in use have been much too low as a result of using too heavy wire for the thermocouple and of not inserting the thermocouple far enough into the rubber. The thermocouple was always much cooler than the mass of the rubber because the leads conducted the heat away more rapidly than it could pass from the hot rubber to the thermocouple through the layer of cooler rubber surrounding the couple. By imbedding the wires for 3.5" in the rubber and using 36-gage wires the true temp. of the rubber can be obtained. Figures and curves to prove the above contention, and cuts to illustrate the most satisfactory method of inserting the thermocouple and encasing the leads are given. E. G. R. ARDAGH

**Nernst's theorem.** TH. DE DONDER. *Bull. sci. acad. roy. Belg.* [v] **8**, 461-5 (1922).—D. obtains various expressions for the heat of reaction at const. pressure, making use of Nernst's theorem. J. C. S.

**Thermodynamics of activity coefficients and osmotic coefficients.** NIELS BJERRUM. *Z. physik. Chem.* **104**, 406-32 (1923).—Several forms of the Gibbs differential equation have been deduced between the affinities of the components of mixts., and it has been shown that these can also be deduced directly from the second law of thermodynamics. The meaning of the Gibbs' equation may be expressed as follows: "during the conversion of a finite quantity of a mixt. into another of infinitesimally different compn. the energy necessary is infinitely small." The different possibilities for the definition of the activity coeff.  $f$  and the osmotic coeff.  $\varphi$  are rendered precise. The deduction and the limit of validity of the equation (previously published):  $1 + C d \ln f / dC = \varphi + C d \varphi / dC$  are discussed, and it is shown that this equation holds up to the highest concns., if the concn. ( $C$ ) is expressed in mols. per l. of solvent and  $f$  and  $\varphi$  are correspondingly defined. If  $f_1$  and  $f_2$  are the activity coeffs. of the solutes  $S_1$  and  $S_2$  contained in the same soln. and  $C_1$  and  $C_2$  their concns., then,  $\delta f_1 / \delta C_2 = \delta f_2 / \delta C_1$ . It is possible to resolve the osmotic pressure of a soln. contg. several solutes into the sum of the partial osmotic pressures. It has not been found possible to det. partial osmotic pressures exptly. by means of semipermeable membranes. H. J. C.

**Electric potential in phase equilibrium.** A. GYEMANT. *Z. physik. Chem.* **104**, 475-80 (1923).—The elec. p. ds. between two phases are always of a thermodynamic nature. Adsorption can alter the course of the potential, but it does not affect the total

p. d. A chain of the type  $\text{Hg} \left[ \begin{array}{c} \text{H}_2\text{O satd. with} \\ \text{Hg}_2\text{Cl}_2 \text{ and } \text{KNO}_3 \end{array} \right] \left[ \begin{array}{c} \text{AmOH satd. with} \\ \text{Hg}_2\text{Cl}_2 \text{ and } \text{KNO}_3 \end{array} \right] \text{Hg}$  is not in thermodynamic equil.; accordingly  $\Sigma \pi \neq 0$ ; wherefore it can be concluded that  $\pi_1 = \pi_2$ , but not that  $\pi_3 = 0$ . H. JERMAIN-CREIGHTON

**Design and use of conductance cells for non-aqueous solutions.** J. L. R. MORGAN



AND OLIVE M. LAMMERT. *J. Am. Chem. Soc.* **45**, 1692-1705(1923).—A review and investigation of the most desirable technic for conductance measurements of non-aq. solns. using non-platinized electrodes. C. R. P.

**Concentration cells in methanol.** J. GRANT AND J. R. PARTINGTON. *Trans. Faraday Soc.* (advance proof) 1923.—The voltages of concn. cells of  $\text{AgNO}_3$  dissolved in MeOH have been measured. The agreement between the values so obtained and those calcd. by the aid of the Nernst equation is excellent. The less concordant results of Wilson (*Am. Chem. J.* **35**, 78(1906)) are attributed to exptl. error. C. R. P.

**Electrochemical behavior of bismuth and antimony in alkaline solution.** G. GRUBB AND F. SCHWEIGARDT. *Z. Elektrochem.* **29**, 257-64(1923).—Bi dissolves anodically in alk. soln. in the form of trivalent ions with the formation of solns. of alkali bismuthite. In this way solns. contg. as high as 1 g. per l. in concd. NaOH or KOH can be obtained. When this concn. is attained, the anode becomes passive as a result of the formation of a coating of a colored higher oxide of Bi. In KOH, Sb dissolves from the anode in the form of trivalent ions. Concd. solns. of K antimonite can be obtained without the passivification of the anode. Passivity occurs with high c. ds., the electrode becoming coated with a layer of white oxide. Although a  $\text{KSbO}_3$  soln. is so strong a reducing agent that it actively absorbs  $\text{O}_2$  from the air, its electrochem. oxidation to  $\text{KSbO}_4$  at a smooth Pt anode is not a reversible process. It can be shown that the formation of  $\text{KSbO}_4$  is not brought about by direct anodic oxidation, but is effected by the  $\text{O}_2$  evolved at the anode. The potential of the process,  $\text{Sb} + 4\text{OH}^- + 3\text{e}^- \rightarrow \text{SbO}_2^- + 2\text{H}_2\text{O}$ , in 10 N KOH at  $20^\circ$  is  $E = -0.675 + (0.058/3) \log C_{\text{SbO}_2^-}$ ; that of the process,  $\text{SbO}_2^- + 2\text{OH}^- + 2\text{e}^- \rightarrow \text{SbO}_3^{2-} + \text{H}_2\text{O}$  is  $E = -0.589 + (0.058/2) \log C_{\text{SbO}_3^{2-}}/C_{\text{SbO}_2^-}$ . From these values the potential of Sb against a soln. contg. 1 g.-ion of  $\text{SbO}_2^-$  in 10 N KOH at  $20^\circ$  is calcd. to be  $E_A = -0.641$  v. H. JERMAIN CARRINGTON

**Electrolytic oxidation of formic acid.** ERICH MÖLLER. *Z. Elektrochem.* **29**, 264-74(1923).—The electrolysis of  $\text{HCO}_2\text{H}$  has been studied at  $20^\circ$  and  $75^\circ$  with anodes of smooth Pt, Pd and Ir and also of these metals coated with the metal-black and the spongy metal. With gradually increasing polarization potentials, oxidation of the acid to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  first takes place at low anode potentials, then suddenly ceases and sets in again at higher potentials. This behavior is ascribed to ability of oxidation to take place in 2 ways. Oxidation by the first of these ways can only occur in the presence of a metal catalyst (anode) and requires the smaller potential. The second way, requiring the higher potential, only takes place when the metal of the anode becomes coated with oxide. Oxidation of  $\text{HCO}_2\text{H}$  to  $\text{CO}_2$  and  $\text{H}_2$  has not been established. H. J. C.

**Contact potentials.** SHIRO TAKEGAMI. *J. Chem. Soc. Japan* **44**, 457-82(1923).—T. assumes that if the e. m. f. of a cell is plotted as abscissa and the concn. of an ideal liquid junction as ordinate, the curve should become vertical from a point where contact potentials become zero. Three types of liquid junctions were tried: (I) KCl and  $\text{KNO}_3$  solns. mixed in the ratio of 81.87 mol. : 18.13 mol., which was calcd. on the basis of equal ionic velocity. In this type, 3 mixts. (in moles per l. of KCl and  $\text{KNO}_3$ , resp.) were used: (1) 3.884, 0.852; (2) 2.574, 0.568; (3) 1.283, 0.284. (II) In the second type, 4 mixts. of  $\text{NH}_4\text{NO}_3$  and LiCl, which have equal ionic velocity when mixed in ratio 89.93 mol. : 10.07 mol., were used (in moles per l. of  $\text{NH}_4\text{NO}_3$  and LiCl, resp.): (4) 8.39, 0.94; (5) 5.59, 0.63; (6) 4.20, 0.47; (7) 2.10, 0.24. (III) The 3rd type was that of greatly concd. liquid junction, in which (8) 8.39 N  $\text{NH}_4\text{NO}_3$  and (9) 6.29 N  $\text{NH}_4\text{NO}_3$  were used. By the usual method, the e. m. f. of  $\text{Hg}|\text{Hg}_2\text{Cl}_2|1 \text{ N KCl}-\text{a liquid junction}-1 \text{ N}|\text{HCl}|\text{Hg}_2\text{Cl}_2|\text{Hg}$  was measured. On account of its changes on standing, the p. ds. found at various times were plotted against the time of measurement and the initial value (0 hr.) was calcd. by extrapolation. The results for the 9 liquid junctions at  $25^\circ \pm 0.01^\circ$  are given in v. as follows:—(1)  $0.0065 \pm 0.00035$ ; (2)  $0.0131 \pm 0.00047$ ; (3)  $0.0258 \pm 0.00045$ ; (4)  $0.0026 \pm 0.00039$ ; (5)  $0.0029 \pm 0.00020$ ; (6)  $0.0088 \pm 0.00027$ ; (7)  $0.0205 \pm 0.00034$ ; (8)  $0.0018 \pm 0.00029$ ; (9)  $0.0060 \pm 0.00020$ . The curve shows that type I is not concd. enough. The curve of type II junctions becomes parallel to the axis of ordinates at  $-0.0025$  to  $-0.003$  v. Thus the real value of this cell free from contact potential might be  $-0.0025$  to  $-0.003$  v. (?) (cf. Fales and Vosburgh, *C. A.* **12**, 2062). The fact that the curves of group I and II are not exactly the same may be due to the fact that in calcd. mol. ratios for equal ionic velocity, the elec. dissociation was assumed to be the same for all the salts. In detg. the e. m. f. of the cell where electrolytes are not very concd., any group of the above liquid junctions can be used, as the following results (in volts) show for the cell  $\text{Hg}|\text{Hg}_2\text{Cl}_2|.01 \text{ N ZnCl}_2-\text{liquid junctions}-0.1 \text{ N ZnCl}_2|\text{Hg}_2\text{Cl}_2|\text{Hg}$ . 3.5 N KCl gave 0.0550; 4.1 N KCl, 0.0556  $\pm$  0.00022; No. 1 above, 0.0547  $\pm$  0.00028; 10.18 N  $\text{NH}_4\text{NO}_3$ , 0.0544  $\pm$  0.00042; 6.72 N  $\text{NH}_4\text{NO}_3$ , 0.0544  $\pm$  0.00044; and No. 4, 0.0545  $\pm$  0.0003. S. T.

The position of tellurium in the electromotive series. J. KASARNOWSKY. *Z. anorg. allgem. Chem.* **128**, 17–32 (1923).—The Nernst equation is shown to hold for the system  $\text{Te}/\text{Te}_2^{--}$ . The normal potential of the above electrode referred to the hydrogen electrode is  $-0.818 \pm 0.002$  volt, while the normal potential of the electrode  $\text{Te}/\text{Te}^{++++}$  referred to  $\text{H}_2$  is  $+0.549 \pm 0.001$  volt. From these values the function  $(\text{Te}^{++++})/(\text{Te}_2^{--})^2 = K = 10^{-14}$ ; and the function  $(\text{Te}^{++++})(\text{OH}^-)^4/(\text{TeO}_2)^{--} = 3.4 \times 10^{-47}$ .

A. E. STEARN

Amphoteric elements. J. KASARNOWSKY. *Z. anorg. allgem. Chem.* **128**, 33–44 (1923).—From thermochemical data the value  $0.4 \times 10^{-2}$  is obtained for the function  $(\text{Te}^{--})/(\text{Te}_2^{--})$ , giving, with data from the previous paper, the value of  $-0.91$  volt for the normal potential of Te toward the  $\text{Te}^{--}$  ion. Analogously the potential of  $\text{Se}/\text{Se}^{--}$  is found to be  $-0.77$  volt, midway between the corresponding S electrode ( $-0.55$ ) and the Te electrode ( $-0.91$ ). From these values the potential of the  $\text{Po}/\text{Po}^{--}$  electrode is estd. by extrapolation as  $-1.0$  volt. The ion products of the positive and negative ions from the same element are so small (about  $10^{-102}$  for  $(\text{Te}^{++++})(\text{Te}^{--})^2$ ) that at a measurable concn. of either, the oppositely charged ion is practically nonexistent.

A. E. STEARN

Metastability of the "International Weston element" and its unserviceability as a normal element. II. ERNST COHEN AND A. L. TH. MOESVELD. *Z. physik. Chem.* **104**, 403–5 (1923); cf. *C. A.* **14**, 3184.—A discussion of the results of other investigators.

H. JERMAIN CREIGHTON

Phenomenon of electric supertension. II. A. SMITS. *Proc. Acad. Sci. Amsterdam* **26**, 259–65 (1923).—Theoretical discussion of polarization. No data.

C. R. PARK

Application of the theory of magnetism to the calculation of atomic diameters. J. F. T. YOUNG. *Trans. Roy. Soc. Canada* **16**, III, 49–61 (1922).—Attention is directed to the periodic distribution of paramagnetic and diamagnetic properties among the elements arranged in the customary periodic table. A mathematical theory, applicable either to the dynamic or static at. model, permitting at. dimensions of an element to be calcd. from the value of the magnetic permeability is detailed, and the results are applied to calc. the at. radii of 26 elements. The values obtained are of the correct order in all cases.

J. C. S.

Effect of masked anions on the magnetic susceptibility of chromic and chromyl salts. B. CARRERA AND S. PIÑA DE RUBIES. *Anales soc. españ. fis. quim.* **20**, 509–18 (1922); cf. *C. A.* **17**, 20.—Sols. of chromic sulfate which when freshly prepd. give no sulfate reaction undergo change on keeping, whereby elec. cond. and sulfate reaction show a parallel increase. No appreciable variation in magnetic susceptibility, however, is observed. In sols. of chromyl sulfate, on the other hand, an increase in magnetic susceptibility is observed. The change is supposed to consist of two successive unimol. reactions, namely,  $[(\text{SO}_4)_2\text{Cr}_2\text{O}] \longrightarrow \text{SO}_4[\text{SO}_4\text{Cr}_2\text{O}] \longrightarrow (\text{SO}_4)_2[\text{Cr}_2\text{O}]$ . The quant. aspect of these reactions is discussed.

J. C. S.

The evolution of the molecule of chromium hydroxide in water. SUZANNE VEIL. *Compt. rend.* **176**, 1304–5 (1923); cf. *C. A.* **17**, 1179.—The magnetic coeff. of chromium hydroxide and the oxide obtained from this by dehydration depends on the previous history of the system. In all cases studied that of the oxide was about one third that of the corresponding hydroxide per unit Cr. Digesting in hot water or reprecip. after soln. in acid lowers the original value of this coeff.

A. E. STEARN

Paramagnetism of cobalt sulfate in aqueous solution. CHATILON. *Compt. rend.* **176**, 1608–11 (1923).—Sols. of  $\text{CoSO}_4$  prepd. in the cold had an at. moment independent of concn. and, within certain limits, of the temp. and equal to 24.5 magnetons. Sols. prepd. by boiling had an at. moment that varied with the concn. and would indicate carriers of from 24 to 25 magnetons. Sols. with an at. moment of 24.5 may be regarded as the result of the association of carriers of 24 and 25 magnetons. These complexes are destroyed by boiling and an equil., which is dependent upon concn. only, is set up. (Cf. Brant, *C. A.* **15**, 3244.)

BENJAMIN S. NEUBAUSER

Variation of the refractive index of oxygen with pressure, and the absorption of light by oxygen at high pressures. (MISS) H. I. EADIE AND JOHN SATTERLY. *Trans. Roy. Soc. Canada* **16**, III, 63–73 (1922).—Gladstone and Dale's law for the relation of  $n$  to  $d$  has been confirmed in the case of O for pressures ranging from 2.1 to 140 kg. per sq. cm. Evidence for the existence of absorption in O at pressures up to 100 atms., in the regions  $\lambda\lambda$  6285, 5800, and 5350 Å. was not conclusive.

J. C. S.

The colorimetric determination of artificial light sources based on the decomposition of hydrogen iodide solutions. ADOLPHO HACKRADT. *Strahlentherapie* **12**, 843–5; *Chem. Zentr.* **1922**, IV, 1001; cf. *Strahlentherapie* **12**, 1005; *Chem. Zentr.* **1922**, III,

103.—The pptn. of I from a HI soln. under the action of ultra-violet light is used as a basis for estg. the time of exposure in medical ultra-violet light therapy. In place of weighing the pptd. I, a comparison of the color of the soln. with a color standard series is recommended.

C. C. DAVIS

Structural colors in feathers. II. Iridescent feathers. C. W. MASON. *J. Phys. Chem.* 27, 401-47(1913); cf. *C. A.* 17, 2667.—An extended study of 26 iridescent feathers disclosed the fact that the iridescence is caused by thin laminae or films in the barbules which produce interference colors. No structural colors and no surface colors due to selective reflection were identified in the iridescent feathers and the inadequacy of both the structural color theory and the surface color theory was demonstrated. Tests are given for the identification of thin film colors in iridescent feathers.

HARRY B. WEISER

The temperature of the crater of some arc lamp carbons and the radiation of the flame arc between them. F. PATZELT. *Z. tech. Physik.* 4, 66-72(1923). H. G.

### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

The electron in chemistry. J. J. THOMSON. *J. Franklin Inst.* 195, 593-620, 737-85; 196, 1-29, 145-80(1923).—A series of lectures. JOSEPH S. HEPBURN

Recent observations on the relation between electrical and optical phenomena. B. GUDDEN AND R. POHL. *Naturwissenschaften* 11, 348-54(1923).—A review of recent work by G. and P. (cf. *C. A.* 14, 3363; 15, 17, 468, 629, 1856, 2782; 16, 1535, 2806, 3434).

C. C. DAVIS

The effective cross-section areas of noble-gas molecules toward slow electrons. CARL RAMSAUER. *Jahrb. Radioakt. Elektronik* 19, 345-54(1923); cf. *C. A.* 16, 871, 1905.—Later and more accurate expts. substantiate the results previously reported.

D. C. BARDWELL

Origins of the conception of isotopes. FREDERICK SODDY. *Engineering* 105, 660(1923).—A report of a discourse. Also in *Chem. News* 127, 92-5, 103-6; *Nature* 112, 208-13(1923).

NORRIS F. HALL

Attempt to separate the isotopes of chlorine by the method of fractional adsorption. JITSUSABURO SAMESHIMA, KAZUO AIHARA AND TOSHIKAKI SHIRAI. *Sci. Repts. Tohoku Imp. Univ.* 12, 149-54(1923).—See *C. A.* 17, 923.

E. J. C.

Atoms and electrons. A. BOUTARIC. *Rev. gén. sci.* 34, 324-33(1923).—A long abstract of the report of the meeting of the Conseil de Physique held at Brussels, April 1st to 6th, 1921, under the auspices of the Solvay International Physics Institute. Many summaries of recent work are included.

NORRIS F. HALL

A model of the neutral helium atom. A. SOMMERFELD. *J. Optical Soc. Am.* 7, 509-15(1923).—A model is worked out in which the two electrons have elliptical coplanar orbits with their aphelia in opposite directions with one electron at the perihelion while the other is at the aphelion. This model accounts for the diamagnetism as well as other properties of He.

F. O. ANDEREGG

The absolute values of the electrical moments of atoms and molecules. R. D. KLEEMAN. *Science* 57, 747-8(1923).—At the zero abs. the attraction between 2 mol. doublets is given by  $4M^2/r^4$  where  $M$  is the moment of each doublet and  $r$  their distance of sepn.  $L_0 = 8.42 \rho_0 M^2/m_e^2$  where  $L_0$  and  $\rho_0$  are the internal latent heat of evapn. and the density, resp., and  $m_e$  is the abs. mol. wt. of a mol., all at zero abs. Using these equations, K. finds  $M = 10^{-19} \text{ EN}^{1/2}$ , where  $N$  is the at. no. of any atom in the mol. The spacing ( $x$ ) of the representative doublet of an atom decreases with increasing at. wt., and is always less than the at. diameter. Thus  $x$  for the H atom is  $2.09 \times 10^{-10} \text{ cm.}$  (cf.  $0.53 \times 10^{-8} \text{ cm.}$ , the radius of the electron orbit on Bohr's theory).

NORRIS F. HALL

Report on the size of molecules, atoms, and ions, and the methods for their determination. K. F. HERZFELD. *Jahrb. Radioakt. Elektronik* 19, 259-334(1923).—A crit. survey is made of the results from the following methods for estg. the size of mols., atoms, and ions: from equations of state and crit. data, dynamics of mol. friction in gases and liquids, energy considerations of hydration, ionization potentials, heat of evapn., melting points, no. of mols. in a unit surface 1 mol. thick, X-ray detn. of lattice dimensions of crystals, electron orbits from at. models (Bohr), penetrability of gases to slowly moving electrons, and various other less general methods. Crit. data give values which are consistent relatively but are not abs. Crystal-lattice measurements

give the differences in size of ions in the solid state. Collisions by slow electrons show that the size of gaseous mols. is variable with the velocity of the electron, etc. The sizes of atoms, mols. and ions obtained by various methods are tabulated. An extensive bibliography is included.

D. C. BARDWELL

**The constitution of the atom.** A. REYCHLER. *Bull. soc. chim. Belg.* **31**, 411-7 (1922); cf. *C. A.* **16**, 3775.—R.'s previous formula for the calcn. of at. weights from at. numbers,  $A = 2N + \beta N^2$ , is now derived from theoretical considerations, and it is shown that the at. radii of the elements of the He group deduced by extrapolation from Bragg's crystal measurements are proportional to the cube roots of their at. numbers. From a consideration of the energy changes involved when an electron is transferred from one shell to another, R. is able to derive Moseley's frequency formula,  $\nu = \text{const.} (1/m^2 - 1/n^2)(N-b)^2$ .

J. C. S.

**Atomic models with elongated nuclei.** H. TEUDT. *Z. Sauerst. u. Stickst.-Ind.* **14**, 38-41; *Chem. Zentr.* **1922**, III, 461.—In contrast to the ring form of the at. nucleus which has heretofore been assumed as probable, the more stable rod form is defended as more nearly correct. On this assumption the requirements of Born with respect to the cubical symmetry of the ions, conclusions from the periodic system, Moseley's formula and the quantum theory are fulfilled.

C. C. DAVIS

**Derivation of the Röntgen spectra and chemical valences of atomic models with elongated nuclei.** H. TEUDT. *Z. Sauerst. u. Stickst.-Ind.* **14**, 53-5; *Chem. Zentr.* **1922**, III, 461.—By means of the new at. model (cf. preceding abstr.) there are derived (1) all known Röntgen lines, (2) the increase and decrease of the primary valences of 1-4 and of 4-0 in the even series of the periodic system, and (3) the differing behavior of the even and odd series in this system.

C. C. DAVIS

**Radioactive constants; their status in 1923.** STEFAN MEYER. *Jahrb. Radioakt. Elektronik* **19**, 334-44 (1923).—Tables show for U, Th, and Act families the period of half decay, the decay const., the av. life, the initial velocities, the range, the total no. of ion pairs in the path of an  $\alpha$  particle in air, the absorption coeff. for Al and the relative wt. of each element in equil. with 1 g. Ra. The terms radon, acton, and thoron for the corresponding emanations are not used in the tables, but are recognized in a note. The no. of  $\alpha$ -particles emitted per sec. by 1 g. Ra is accepted as  $3.72 \times 10^{10}$ . The no. of ion pairs in the path in air of an  $\alpha$ -particle from Ra C is given as  $2.20 \times 10^5$  in preference to the previous value,  $2.37 \times 10^5$ . Proportional corrections are made for the no. of ion pairs produced by  $\alpha$ -particles from other elements.

D. C. BARDWELL

**The genetic relationship between thorium and uranium and the determination of the age of radioactive minerals.** GERHARD KIRSCH. *Sitz. Akad. Wiss. Wien* **131**, *Abt. IIa*, 551-68 (1922).—The parent of Th is supposed to be a U isotope present in small amts. in all terrestrial U at the time the oldest U minerals were formed, and since completely disappeared. If pure ancient U minerals exist which were originally free from Th and Pb, the half period of "Th U" can be calcd. from the present relative Th/U and Ra G/U ratios of the mineral. From this and the age of the mineral calcd. from its Ra G/U ratio, the present "Th U" content of the U may be inferred, and, conversely, the age of other minerals may be inferred from the ratio of their Th contents, and the results of the Pb and He methods of estg. age may be checked. When the methods are applied first to the bröggerite of Moss and the East African pitchblende (Morogoro ore) the half period  $6.3 \times 10^7$  yrs. is obtained for "Th U." The same value is also obtained from Morogoro ore and St. Joachimsthal pitchblende. Numerous analyses of U and Th minerals are cited and critically studied. It is concluded (1) that in general the Th content increases with the age of the U mineral, as would be expected, (2) that the half life period for Th is  $1.65 \pm 0.05 \times 10^{10}$  years. Many special conclusions concerning the age of particular thorites, thorianites and other minerals are also reached.

NORRIS F. HALL

**The relative ionization along the paths of alpha particles in different gases.** FRITZ HAUBR. *Sitz. Akad. Wiss. Wien* **131**, *Abt. IIa*, 583-7 (1922).—A parallel sheaf of  $\alpha$ -rays was passed through air, O<sub>2</sub>, CO<sub>2</sub>, and impure He, and the ionization measured. The no. of ions produced per unit of distance increases the more rapidly with the distance from the source (Po), the less dense the gas used. It is concluded that the loss of energy of an  $\alpha$ -particle in the production of a pair of ions in a given gas is not given by the necessary work of ionization alone, but that there is to be added to this work a quantity of energy which depends on the speed of the particle and the d. of the gas.

N. F. H.

**Theory of backward diffusion of  $\beta$ -rays.** GREGOR WENTZEL. *Ann. Physik* **70**, 561-594 (1923); cf. *C. A.* **17**, 674, 923.—The backward diffusion of  $\beta$ -rays is treated theoretically from the standpoint of defections due to the kernel of the Rutherford-Bohr at. model. Mathematical deductions are specialized so as to make possible com-

parison with the results of H. W. Schmidt (*C. A.* 2, 753) with which good agreement is obtained. The true absorption coeffs. for  $\beta$ -rays from U X in Al, Zn, Sn, and Pb are evaluated and found to be only approx. proportional to mass. The intensity of backward diffusion depends upon the thickness and material of the plate under the active source as well as upon the thickness and material, the absorption of which is being studied. For const. lower plate, the backward diffusion const. for the material of the upper plate can be evaluated from the strongly convergent power series:  $q_{\infty} = b_1(Z^2\rho/\alpha A) + b_2(Z^2\rho^2/\alpha A) + \dots$ , where  $Z$  = at. no.,  $\rho$  = density,  $A$  = at. wt., and  $\alpha$  = true absorption coeff.  $b_1$  is calcd. upon theoretical grounds to be 0.12 cm.<sup>2</sup>/g., in good agreement with the empirical value, 0.13 cm.<sup>2</sup>/g. from Schmidt's results.

D. C. BARDWELL

**Chemical action of the penetrating radium rays.** XV. The dependence of the action on the part of the radiation absorbed, with a note on the reduction of potassium persulfate. ANTON KAILAN. *Sitzb. Akad. Wiss. Wien* 131, *Abt. IIa*, 589-81(1922); cf. *C. A.* 16, 2806.—The decompn. caused by the rays was measured in acid, neutral, and alk. H<sub>2</sub>O<sub>2</sub>, and in acid KI. Vessels of different forms and sizes and various radiation filters were used. K.'s former assumption that the action is due to the  $\beta$ - and  $\gamma$ -rays in the proportion of the nos. of pairs of ions produced or producible by the absorbed part of each kind of radiation is confirmed. The  $\gamma$ -rays are responsible for a large fraction of the chem. effect. The relative action is increased 30 or 40% by quadrupling the vol. of the vessel but keeping its shape the same (this is due to secondary influences). No increase in speed of the decompn. produced by the radiation alone takes place when a neutral H<sub>2</sub>O<sub>2</sub> soln. is made 0.1 N in Na<sub>2</sub>CO<sub>3</sub>. In the reduction of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> caused by the rays, the no. of the reduced mols. is of the same order as the no. of pairs of ions produced. Also in *Monatsh.* 44, 35-47(1923). NORRIS F. HALL

**The secondary electronic radiation caused by the gamma rays of radium.** ALFONS ENDRELE. *Sitzb. Akad. Wiss. Wien* 131, *Abt. IIa*, 589-605(1922).—Elements of high at. wt. were used as absorbers. The  $\gamma$ -components of different hardnesses each liberate a special type of secondary electrons, whose initial velocity depends on the wave length of the  $\gamma$ -rays. Each type of secondary rays has its own asymmetry coeff. (As-C) (ratio of the emergence to the incidence radiation) (cf. Bragg and Madsen, *C. A.* 3, 986) and the harder types have the larger As-C's. The anomalous reversal of the asymmetry in Pb is an absorption effect, which is common to all elements with high at. wt. and with plates of Pb 0.5 mm. thick makes the apparent (measured) As-C < 1. From the ranges of the incidence and emergence radiation are calcd. the absorption coeffs. of the types of electrons dislodged by the principal  $\gamma$ -components, and it is shown that  $\mu/\rho = f(A)$ , where  $A$  is at. wt., in general increases for these rays just as for the  $\beta$ -rays of U X. True As-C's are calcd. for Pb, Au, Ni, and Fe. These converge toward 1 when plotted as a function of the at. wt.

NORRIS F. HALL

**The change of charge of hydrogen positive rays.** E. RUCHARDT. *Ann. Physik* 71, 377-423(1923).—The paper gives a mathematical discussion of the underlying theory and the exptl. detn. of the change of charge of H positive rays in H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>.

M. FARNSWORTH

**The work of Günther-Schulze on the energy distribution at the cathode in the glow discharge.** R. SREILIGER. *Z. Physik* 16, 211-14(1923); cf. *C. A.* 17, 2338.—The calcs. of G.-S. are shown to lack agreement with his own as well as numerous other expts. Serious objections are raised to the G.-S. assumption of high temp. in the dark space.

F. O. ANDEREGG

**Disruptive potentials in gases at elevated pressures and the molecular field.** II. C. E. GUYE AND J. J. WEIGLE. *Arch. sci. phys. nat.* 5, 85-96(1923); cf. *C. A.* 17, 2386.—The flowing gas method gave results in N somewhat similar to those in CO<sub>2</sub>. The mobility of the ions in N was much the greater since they diffuse laterally while calcs. are made which show that the mol. field of CO<sub>2</sub> causes its ions to tend to stay in the interpolar axis resulting in numerous collisions.

F. O. A.

**Term structure and Zeeman effect in multiples.** A. LANDÉ. *Z. Physik* 15, 189-205(1923).—Making use of new exptl. material on Mn (cf. following abstract) and Cr, L. gives rules whose application yields rather simply a comprehensive description of the empirical situation in regard to spectral terms of all degrees of complexity (singlets, doublets, . . . octets). Application of appropriate selection rules then gives the entire set of possible spectrum lines resulting from combinations of such terms. An additional equation then gives for every individual term the proper factor  $g$  by which the normal Zeeman displacement  $\Delta\lambda_{\text{norm.}}$  must be multiplied; the actual Zeeman effect for each term is then  $mg\Delta\lambda_{\text{norm.}}$ , where  $m$  is the magnetic quantum no. The Zeeman pattern or type for each (type of) spectral line is then given by appropriate

combinations of such terms. For a complete specification of the rules and equations, reference must be made to the original. A table is given presenting the values of  $g$  for all possible terms, for values of the azimuthal quantum no. up to 5. A general "interval rule" holds more or less closely for the ratios of the frequency intervals between successive components in any complex term. Tentative explanations are given of the preceding empirical generalizations in terms of vector combinations of the angular momenta of the atom core ("Rumpf") and of the outer electron. Heisenberg's assumption (*C. A.* 16, 3032) of two core quantum nos. is unjustified. L.'s empirical generalizations also do not agree with some of H.'s ideas, which were based on less complete data.

R. S. MULLIKEN

**Zeeman effect in the arc and spark spectrum of manganese.** I. E. BACK. *Z. Physik* 15, 206-43(1923).—B. has made a detailed study of the Zeeman types for most of the multiplets found by Catalán (*C. A.* 17, 1586) and for a *new quadruplet*. The results are in complete agreement with the theoretical treatment of Landé (cf. preceding abstract), which is to a considerable extent based on B.'s data. The intervals in the multiplets also furnish confirmation of L.'s interval rule. B. shows, in part by the help of the interval rule, that the spark spectrum of Mn agrees exactly in type with the arc spectrum of Cr as analyzed by Gieseler (*C. A.* 17, 683); this confirms the Sommerfeld-Kossel alternation law, and is contrary to Catalán's idea that the arc and spark spectra of Mn are of similar type. A list of references to work on the Zeeman effect in the Mn spectrum is given.

R. S. MULLIKEN

**Paramagnetism and the structure of the atom.** A. DAUVILLIER. *Compt. rend.* 176, 1802-5(1923).—Paramagnetism is due to two distinct causes: the external and the internal electrons. Sometimes these work together, sometimes separately. The groups of atoms Ti-Cr, Ti-Mo, Cr-W and Th-U are paramagnetic because of the external electrons. The groups Mn-Ni, 43-Pd, 75-Pt, and Ce-Lu are paramagnetic because of incomplete layers. The groups Si-S, Ge-Se, Sn-Te, etc., have the same external structure as Ti-Cr but are diamagnetic because of their electronegative character. The variations in magnetic moment from element to element are integral multiples of the Weiss magneton. D. calcs. the magnetic moments of the members of the series Sc-Cu, assuming that this moment is due to the M and N layers. The structure assumed is only partly in accord with Bohr's at. model. For heavier atoms layers farther from the nucleus have similar effect.

F. J. BROWN

**The bending of X-rays in microcrystalline structure.** N. USPENSKI AND S. KONOHEJWSKI. *Z. Physik* 16, 215-27(1923).—X-ray photographs of crystals turned at different angles show interesting patterns from which lattice structures may be calcd. The agreement with other methods is good for Al and Cu. Pt has a similar lattice structure with a parameter of 3.87 Å. Fe gives too complicated a pattern to allow calcn. of its structure. Ni and Ag exhibit a combination of the Al and Fe types of structure.

F. O. ANDEREGG

**Intensity distribution and the origin of the band spectrum of nitrogen.** H. KIRSCHBAUM. *Ann. Physik* 71, 289-316(1923).—K. has investigated the effect of pressure, current density, temp., and nature of discharge, on the intensity distribution in a no. of bands of the second positive and of the negative group of N, between the wave lengths 3900 and 4700. Some work has also been done on bands of longer wave length. Low-dispersion photographs, taken with a special spectrograph designed to give max. illumination, were measured microphotometrically. Four types of discharge tube were used. The rate of decrease of intensity from near the band head became less (and the individual lines—far from the head—became more prominent) with increase of either pressure, temp., or current-density. The effect was shown to be probably primarily due to temp. in all 3 cases. The spectrum as excited by canal-rays, as compared with that of the positive column or negative glow, was also of the high-temp. type. The effect of either temp. or of the massive positive rays is to excite mol. vibration, while the cathode rays in the discharge affect chiefly the electrons in the N<sub>2</sub> mols. [The type of temp. effect here observed has been simply explained (as due to increase in no. of mols. having large *rotational* quantum nos.) in terms of the quantum theory, which K. does not make use of.—ABSTR.] Some observations were also made on relative total intensities of different bands, and considerable effects were found with high temp. or by use of positive rays.

R. S. MULLIKEN

**Mode of absorption of triphenylmethane coloring matters.** E. ADINOLFI. *Atti acad. Lincei* [v] 31, ii, 551-4(1922).—Consideration of the various theories advanced to establish chemico-phys. connections between constitution and absorption, together with the results previously obtained (*C. A.* 17, 1379), shows that triphenylmethane coloring matters, in soln. in water or in Me, Et, isobutyl, or Am alc., give rise to ab-

sorption spectra of similar type, and with maxima which undergo increasing displacement as the mol. wt. of the solvent increases. To this rule, rhodamine-B and uranine form exceptions, probably owing to reëmission resulting from fluorescence. The two characteristic absorption bands of these coloring matters are due to two distinct vibrators, which in some cases diffuse with unequal velocities, and in others disappear alternately in acid or alk. solns., and undergo displacements to different extents in different solvents. J. C. S.

**The spectrum of neutral helium.** C. V. RAMAN AND A. S. GANESAN. *Astrophys. J.* 57, 243-7 (1923). The spectrum of neutral helium, a rejoinder to C. V. Raman and A. S. Ganesan. LUDWIK SILBERSTEIN. *Astrophys. J.* 57, 248-50 (1923).—R. and G. question the validity of Silberstein's formula for the lines of neutral He (C. A. 17, 238, 364) on the grounds of ionizing potential and series relations, and contend that the coincidences are due to chance agreement. S. points out that the formula covers many of the combination lines. He prefers a more extensive treatment of the ionizing potential, and shows that there is small chance that the coincidences are fortuitous if the nos. involved are kept sufficiently small. K. BURNS

**The band spectrum of iodine.** R. МЕРКА. *Ann. Physik* 71, 104-34 (1923).—After new measurements between 5000 and 7150 Å., M. arranges the band heads in the absorption spectrum of iodine in 10 series. The longest series begins and ends in the region of shorter wave lengths; succeeding series are progressively shorter and lie more toward the red. The entire system of bands is satisfactorily correlated by an empirical formula; the correct values of the initial and final vibrational quantum nos.,  $n_1$  and  $n_2$ , are uncertain, but a likely formula in terms of these is given. The iodine band system is very different from the CN and similar systems; there is a great variety of values of  $(n_1 - n_2)$ , and the values of  $n_2$  are much higher (not approaching 0), and more varied, for low values of  $n_1$  (region of shorter wave lengths) than for higher values (red region). The  $n_1 n_2$  diagram is bounded by approx. hyperbolas ( $n_1 n_2^2 = \text{constant}$ ). M. has previously given (C. A. 16, 2262) equations for the resonance doublet series excited in I vapor by the Hg green and yellow lines, as observed by Wood. He now relates these in part to the absorption spectrum. By analysis of a photograph of Wood's, he detcs. a doublet series belonging to one of the absorption bands, and including 4 lines which give rise to resonance series. Other resonance lines are tentatively assigned to 3 other absorption bands. M. has measured the lines of 4 of the absorption bands in the red. (Other bands showed similar structure.) In each case the lines can be expressed in a single Deslandres series (the first 30 lines near the head are, however, not resolved). M. thinks this is a Q series, in terms of the quantum theory of band spectra, and that the P and R series are lacking. R. S. MULLIKEN

**The band spectrum of carbon monoxide.** E. HULTHÉN. *Ann. Physik* 71, 41-9 (1923).—H. has arranged the lines of each of the CO bands at wave lengths 5610, 5198, 4835, and 4393, in 3 series, corresponding to typical P, Q, and R branches of the quantum theory. The theoretical relation  $R(m) - Q(m) = (m + 1) - P(m + 1)$  is accurately verified. The values of  $R(m - 1) - Q(m)$  and of  $Q(m) - P(m)$  show that the last 2 of the above bands have the final vibrational state (probably  $n = 0$ ) in common, while 4835 has the initial state (probably  $n' = 2$ ) in common with the remaining 2 bands, and with 2 additional bands in the red whose structure has not yet been detcd. An expression is detcd. for the energy of the rotation term in the initial and final states. R. S. MULLIKEN

**Vacuum spark spectrum of silicon.** R. A. SAWYER AND R. F. PATON. *Astrophys. J.* 57, 279-93 (1923).—See C. A. 17, 2236. E. J. C.

**The arc spectrum of cerium.** JACQUES BARDET. *Compt. rend.* 176, 1711-12 (1923).—B. has examd. the spectrum of the arc of Ce produced with C electrodes and has tabulated the readings made over the region 2300 to 3500 Å. L. T. FAIRHALL

**Pole effects, pressure shifts, and measurements of wave lengths in the spectrum of manganese.** G. S. MONK. *Astrophys. J.* 57, 222-33 (1923).—A correspondence was found between the pole effect and the pressure shift of unsym. lines. The pole effect is small when  $\text{MnCl}_2$  is used, and moderately large when the oxide is used to charge the lower C. For wave lengths, the central mm. of a 12-mm., 5-amp., 220-v. arc was observed by means of interferometers of 5 and 7.5 mm. thickness. By means of lines of Ne and of group "a" of Fe, the wave lengths of about 40 Mn lines were observed with a probable error of 0.002 Å. in the region 4470-6021 Å. K. BURNS

**Destruction of the fluorescence of dilute solutions by ultra-violet light.** (Miss) F. M. CALK. *Trans. Roy. Soc. Canada* 16, III, 257-63 (1922).—Detns. have been made of the decrease of fluorescence of a dil. aq. soln. of esculin by exposure to ultra-

violet light. After the soln. was once exposed, its fluorescence continued to decay even when the soln. was kept in absolute darkness. On subsequent exposure of the soln. to ultra-violet light, the rate of decay decreased very rapidly at first, then steadily. On further exposure, after an interval of several hours, the rate of decay was greater than before the interval. Ozone bubbled through the soln. caused a very rapid decay of the fluorescence, the soln. finally possessing the same color and absorption spectrum as that transformed by ultra-violet light. J. C. S.

**Cells of fluorescent liquids.** M. A. GRUNMACH. *Compt. rend.* 176, 88–90(1923).—Two electrodes placed in a fluorescent soln. form a cell if one or the other electrode is illuminated. The e. m. f. varies with the time. The phenomenon does not have its origin at the surface of the electrodes since the latter may be immersed in a suitable soln. in the dark and an e. m. f. is set up by pouring around one electrode a small amt. of the same soln. exposed for some time to the light of a Hg arc. Expts. with a 0.05% soln. of pure uranine showed that the lighted electrode was negative at first. The e. m. f. increased to a max. of 8.2 milliv. in 21.3 min. and finally changed in sign, reaching a value of 108.3 milliv. in 144 min. By use of a color filter which allowed only the green radiation of the Hg arc to pass, an e. m. f. of —18 milliv. was attained in 8.2 min. The phenomenon thus serves as an extremely delicate test of the decompn. of colored materials by light. The electrodes adsorb the photo product, whose diln. is very great so that a true concn. cell is formed. HARRY B. WEISER

**Photochemistry of potassium permanganate. II. Energetics of the photo-decomposition of potassium permanganate.** E. K. RIDGAL AND R. G. W. NORRISH. *Proc. Roy. Soc. (London)* 103A, 366–82(1923); cf. *C. A.* 17, 2677. —An absorption spectrum band of  $\text{KMnO}_4$  was located between the limits 380 and 270  $\mu$ , with its head at 313  $\mu$ , while beyond 260  $\mu$  a second band commenced. The visible radions of the Hg-vapor spectrum are not appreciably effective in the decompn. of  $\text{KMnO}_4$ . Reasons are given for considering the line at 312.8  $\mu$  as the chief agent in the photo-decompn. by the Hg-vapor light. The absorption of radiant energy by  $\text{KMnO}_4$  was measured quant., and with certain assumptions as to the active wave lengths, it was shown that 2 quanta are probably concerned in the photo decompn. of the  $\text{MnO}_4$  ion. The photosensitivity of mixts. of  $\text{KMnO}_4$  and  $(\text{CO}_2\text{H})_2$  was examd. by the potentiometer method, and it was shown that such mixts. are much more sensitive to ultra-violet light than to visible light. The mechanics of the photo-decompn. of the  $\text{MnO}_4$  ion is discussed in the light of the exptl. data. E. P. WIGHTMAN

**Formation of organic compounds from inorganic by the influence of light.** OSKAR BAUDISCH. *Science* 57, 451–6(1923).—The role which traces of Fe play in the reduction of nitrates is considered. The surprising fact was observed that nitrates are reduced instantaneously in the presence of O and ferrous salts. Many reactions are brought about by the "fertilization" of the Fe mol. by mol. O. The labile intermediate product  $\text{K}(\text{NO})$ , produced in the reduction of nitrates with light or with  $\text{Fe}(\text{OH})_2$  and O, reacts

very rapidly with aldehydes to form *hydroxamic acids*,  $\text{R} \cdot \text{C} \begin{smallmatrix} \nearrow \text{NOH} \\ \searrow \text{OH} \end{smallmatrix}$ . Another intermediate product,  $\text{H}_2 \cdot \text{C} \begin{smallmatrix} \nearrow \text{OH} \\ \searrow \text{NO} \end{smallmatrix}$ , is likewise formed by the reaction of some *nitrosyl* with

the aldehyde. The stable product of the reaction, however, is *formhydroxamic acid*, stable in the dark but partially rearranging in the light into *acetyl-methylmethane*,  $\text{H}_3\text{C} = \text{N} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}$ . The similarity of these reactions to those caused by soil bacteria is discussed.

There is as yet no basis for assuming that the formation of  $\text{HCHO}$  from  $\text{CO}_2$  of the air and sunlight can be carried out at sea level without the aid of chlorophyll, although the synthesis of formhydroxamic acid from  $\text{N}_2\text{O}$  and  $\text{HCHO}$  has been carried out at high altitudes, and the latter has been produced from  $\text{CO}_2$  under the influence of light of very short wave length ( $\lambda = 200\mu$ ), or of the silent elec. discharge. E. P. W.

**Photochemistry of unstable substances.** E. J. BOWEN. *J. Chem. Soc.* 123, 1199–1206(1923).—The photochem. decompn. of  $\text{CCl}_4$  solns. of  $\text{ClO}_2$  and of  $\text{Cl}_2\text{O}$  under influence of violet light appears to agree with the law of the photochem. equivalence. Solns. of  $\text{NCl}_3$  in similar circumstances give less certain results not far removed from the requirements of the law. E. P. WIGHTMAN

**Sublimation of some substances (in the light) (PURGOTTI) 2. Rhotropism (STOBER) 10.**



## 4—ELECTROCHEMISTRY

COLIN G. FINK

**Electric furnace melting practice.** E. G. STEDMAN. *Trans. Am. Soc. Steel Treating* 3, 740-5(1923).—A comparison of elec. furnace vs. open-hearth equipment together with a description of operations at the Timken Roller Bearing Co. W. A. MUDGE

**Selection of electric furnace for steel treating.** C. L. IPSGRN. *Trans. Am. Soc. Steel Treating* 3, 720-8(1923).—Improved design, automatic control, and favorable atm. conditions make the elec. furnace more economical than furnaces fired with gaseous, liquid or solid fuels when a high-grade material is desired. W. A. MUDGE

**Development of electrolytic iron.** R. J. TRAILL. *Can. Chem. Met.* 7, 181-2 (1923).—Tubes and sheets are produced electrolytically by the use of a revolving cathode in a neutral soln. of ferrous salts, which is circulated about the anode, or by steel turnings with cast iron as anode. Introduction of air into the soln. causes the formation of oxychloride of Fe which absorbs the H liberated at the cathode. The c. d. may reach 100 amp. per sq. ft. and the temp. 75°. The resulting iron from pig iron anodes averages: 0.004% C, 0.007% Si, 0.006% S, and 0.008% P. The metal is hard, very brittle, and contains occluded or combined gases, which are removed by slight annealing. Tubes made by the electrolytic process have better thermal cond., are more resistant to corrosion, and have greater strength than fused metal tubes. The direct application to sulfide ores is discussed; it has commercial possibilities. W. H. BOYNTON

**The effect of temperature on overvoltage.** M. KNOBEL AND D. B. JOY. *Trans. Am. Electrochem. Soc.* 44, preprint(1923).—In an attempt to obtain complete overvoltage density curves, measurements were made by varying the temp. of  $H_2 | 2 N H_4 S O_4 | H g - S O_4 | H g$  cell from 0° to 90°. On returning to lower temps., inconst. values were obtained. By increasing the speed of change from low to high temps. fair checks were obtained. App. is described. Results are given for hydrogen overvoltages at various temp. and current densities, with electrodes of Ag, Cu, Pb and Pt. Straight line curves of overvoltage were obtained in most cases, with occasional hysteresis. No theory is presented to explain the behavior and results. A. H. DICK

**The (British) accumulator industry.** ANON. *Beama* 13, 131-7(1923).—An illustrated review. C. G. IF.

**The disappearance of gas in electric discharge.** ANON. *Trans. Am. Electrochem. Soc.* 44, preprint(1923).—Experiments were carried out with evacuated incandescent tungsten lamps. Results indicate that the disappearance or "clean up" of the residual gases by phosphorus is due to the adhesion of the gas to a film of solid deposited by the discharge on the walls of the container. Other substances behave similarly to phosphorus. The inactive gases are more difficult to eliminate than gases such as oxygen or CO<sub>2</sub> and a possible explanation to account for this difference is suggested. C. G. F.

A new application of the electric furnace (BRISAUD) 20.

**Sectional electric resistance furnace.** E. L. SMALLEY. U. S. 1,463,559, July 31. Furnace sections are arranged end to end with a common resistor for all the sections. Cf. C. A. 17, 2838.

**Rotatable electric resistance furnace.** C. L. LEE. U. S. 1,463,513, July 31. The furnace is adapted for use in welding Cu fins, for cooling, on cylinders of internal-combustion engines.

**Electric-furnace linings.** W. R. CLARK. U. S. 1,461,862, July 17. In starting an induction furnace, a composite body formed of materials of different m. p., e. g., paraffin and Cu or brass cloth, is placed within the heating space of the furnace and the materials are successively melted in starting the furnace, e. g., to melt brass. U. S. 1,461,863 relates to mechanical features of prep. linings of elec. furnaces.

**Dry battery.** W. R. LOVEMAN. U. S. 1,462,795, July 24. Two sep. portions of different depolarizing material are used having different depolarizing values, e. g., mixts. of ordinary and of extra high efficiency.

**Galvanic batteries.** O. NEUMANN and A. NEUMANN. Brit. 191,358, Feb. 15, 1922. Addn. to 184,762 (C. A. 17, 29). The alloy used for making storage battery electrodes described in the principal patent is modified by the substitution of K for Na, and the addn. of W. KOH is used instead of NaOH in the cathode and anode pastes and KHSO<sub>4</sub> is substituted for Na<sub>2</sub>SO<sub>4</sub> and Zn(OH)<sub>2</sub> in the cathode paste to which is also added HgSO<sub>4</sub>. Th<sub>2</sub>SO<sub>4</sub> is added to and Na<sub>2</sub>SO<sub>4</sub> omitted from the anode paste.

**Electrolytic concentration of metals of the chromium group.** R. E. PEARSON and E. N. CRAIG. U. S. 1,462,421, July 17. Cf. C. A. 16, 3267; 17, 693. An anode is surrounded with crude W or similar material to be purified and with  $\text{H}_2\text{SO}_4$  or other electrolyte in which the metalliferous material is insol. but in which the oxy compds. of Na, Fe and Mn or other anode products to be isolated are sol. and the materials are electrolyzed in order to purify the W or other material treated. Crude molybdenite or wolframite may be treated with  $\text{H}_2\text{SO}_4$  and NaOH electrolyte, resp.

**Electrolytic condenser.** L. W. CHUBB. U. S. 1,463,152, July 31.

**Apparatus for electrical precipitation of suspended particles from gases.** C. H. WEISKOPF. U. S. 1,463,352, July 31; cf. C. A. 17, 2240.

## 5—PHOTOGRAPHY

C. E. K. MEES

**The gelatin emulsion and the latent image.** P. F. RENWICK. *Brit. J. Phot.* 70, 382(1923).—A review is given of various theories and phenomena associated with the latent image. R.'s theory is based on the belief that Ag in the charged colloidal condition is present in the solid soln. composing an emulsion and that it is rendered neutral (loses its negative charge) when exposed to light. This change results in the formation of nuclei made up of submicrons of neutral Ag which in turn catalyze the reducing action of the developer on the Ag halide. This theory appears to be the most satisfactory explanation of several other phenomena associated with the latent image. The article concludes with a review of recent methods of studying the mechanism of the action of light on emulsions with special reference to the work of Svedberg.

C. E. K. MEES

**The Raylo process of color photography.** J. W. GANNON. *Camera Craft* 30, 306-10(1923).—This is a three-color subtractive process using an automatic camera. Three successive exposures (each  $1 \times 1\frac{1}{2}$  in.) are obtained on a single  $1\frac{1}{4} \times 3\frac{3}{4}$  in. plate in from  $\frac{1}{4}$  to 30 sec. upon releasing the mechanism. The finishing is done by the Raylo Corporation by projecting the images on sheets of pigmented dichromated gelatin which are developed by washing in water and then dried and transferred by stripping to a sheet of paper to produce the finished print.

C. E. K. MEES

**A new method of dye toning.** M. ROBACH. *Brit. J. Phot.* 70, 363-4(1923).—A dye toning process employing  $\text{H}_2\text{S}$  as the mordanting agent is described. The image is first bleached with the following bath:  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  80 grains, NaCl 160 grains,  $\text{HCl}$   $\frac{1}{2}$  oz., water to 64 oz. It is then rinsed and immersed in a clearing bath of 3%  $\text{NaHSO}_3$ . Three re-developing formulas are given; the first two contain sulfide as the active agent, and the third contains  $3\text{Na}_2\text{S}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$  (Schlippe's salt). Subsequent washing, dyeing and dye clearing operations are described, formulas being given. A list of dyes and combinations of dyes for producing different effects and instructions for double toning are given. The process encourages correct and even dyeing of both high lights and shadows, and fixation after dyeing to obtain transparency is unnecessary.

C. E. K. MEES

**A double surface half-tone plate.** S. H. HORGAN. *Inland Printer* 71, 373-4 (1923).—A plate in which the high lights are depressed thus obviating overlay is said to have been developed by Powers Engraving Company.

C. E. K. MEES

**Photographic development.** R. KELLER. *Kolloid-Z.* 32, 394-7(1923).—The developing agent in a photographic developer soln. is necessarily either an anion or a negative colloid. Exptl. evidence in support of this conclusion is given.

C. E. K. M.

## 6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

**An intercepted hydrolysis.** O. D. DE C. ELLIS and L. B. GIBBONS. *J. Am. Chem. Soc.* 45, 1727-8(1923).—An attempt to form  $\text{PH}_4\text{CN}$  by heating KCN, P and  $\text{H}_2\text{O}$  in a H atm. gave pure  $\text{NH}_4\text{CN}$ . The P prevented complete hydrolysis of KCN to  $\text{NH}_3$  and  $\text{HCO}_2\text{K}$  by reacting with the KOH first formed. Al powder also produced very pure  $\text{NH}_4\text{CN}$ , and the yield was greatly increased by addn. of  $\text{H}_2\text{SO}_4$ .

C. C. DAVIS

**Preparation of metallic sulfides by double decomposition.** Application to cuprous sulfide. GERMAINE MARCHAL. *Bull. soc. chim.* 33, 597-602(1923).—The reaction

$\text{Sb}_2\text{S}_3 + 6\text{Cu} = 3\text{Cu}_2\text{S} + 2\text{Sb} + 26.4 \text{ cal.}$  was studied by heating in a vacuum furnace a mixt. of very pure stibnite and powdered Cu. The reaction was complete after 4 hrs. at 600–700°. With proportions to produce the reaction  $3\text{Cu} + \text{Sb}_2\text{S}_3 = 3\text{CuS} + 2\text{Sb} - 4.5 \text{ cal.}$ , there is formed  $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ , m. 570°, decomp. at 580°; it can be obtained fairly pure at 530°. Above 580° it evolves  $\text{Sb}_2\text{S}_3$  and  $\text{Cu}_2\text{S}$  is formed. No  $\text{CuS}$  can be obtained. The reaction  $\text{ZnS} + 2\text{Cu} = \text{Cu}_2\text{S} + \text{Zn} - 22.7 \text{ cal.}$  could be realized at 960° in the same app. with both native blende, Fe-free, and artificial sulfide.

A. R. M.

**Reaction of ferric salts with alkali thiocyanates.** J. F. DURAND AND K. C. BAILEY. *Bull. soc. chim.* 33, 654–9 (1923).—Expts. are described, with solns. of  $\text{Fe}(\text{NO}_3)_3$  or  $\text{FeCl}_3$  and  $\text{KSCN}$  and  $\text{Et}_2\text{O}$  or  $\text{AmOH}$ , which show that the org. solvents dissolve Fe only when  $\text{KSCN}$  is in excess; if Fe salt is in excess little or no Fe passes from the aq. layer. It is concluded that  $\text{Fe}(\text{SCN})_3$  is insol. in these solvents in the presence of water and that in the two-phase system two compds. are formed of which one dissolves in the org. solvent with violet-red color while the other,  $\text{Fe}(\text{SCN})_3$ , remains entirely in the aq. layer. KI and alkali acetates give red solns., the former with both org. solvents, the latter with  $\text{AmOH}$  only. A red color produced by ferric salt, even in the presence of  $\text{HCl}$ , is not decisive evidence of thiocyanate even if it is absorbed by  $\text{Et}_2\text{O}$  or  $\text{AmOH}$ . The colorimetric method proposed by Lachs and Friedenthal (*C. A.* 5, 2380), while possibly accurate for Fe, certainly cannot be used analogously for detn. of thiocyanate.

A. R. MIDDLETON

**Ammonia and carbonates of the potassium group.** H. PAULY. *Ber.* 56B, 1454–5 (1923).—When the anhyd. neutral carbonate of K, Rb or Cs is added to an aq. soln. of  $\text{NH}_3$  of any concn. at a temp. below 20°, rise of temp. being prevented by external cooling, at satn. two layers form, the upper contg. within 1% of all the  $\text{NH}_3$  and the lower within 1% of all the carbonate. Water of neither layer is at the disposal of the other layer. If to this system a little  $\text{Cu}(\text{AcO})_2$  is added, all the Cu, except traces, dissolves in the lower layer. If the carbonate layer is not completely satd., addn. of Cu salt causes the layers to coalesce but upon further addn. of carbonate to satn. sepn. of the layers again takes place, practically all the Cu being in the lower layer. Copper can thus be removed from  $\text{NH}_3$  soln. by shaking with solid  $\text{K}_2\text{CO}_3$  to satn. Similarly *cellulose* in soln. in Schweizer's reagent can be sepd. and if  $\text{NH}_3$  is allowed to evap. from the upper layer, a thick sirupy soln. is obtained which is well suited for prepn. of osmotic app.

A. R. M.

**Study of metallic oxides and their hydrates by X-rays. I. X-ray analysis of stannic oxide.** NABUO YAMADA. *J. Chem. Soc. Japan* 44, 210–9 (1923).—In order to det. the causes of the existence of  $\alpha$  and  $\beta$  forms of  $\text{H}_2\text{SnO}_3$ , Y. prepd. the oxide by various methods and compared it with the natural (Naegi product) cassite rite by means of an X-ray photograph (Debye and Scherrer's method). Ten samples were prepd. by methods of (1) Zsigmondy, (2) Schneider, (3) Collins and Wood, from  $\text{SnCl}_4$  and marble ( $\text{SnO}_2 \cdot 4.2 \text{ H}_2\text{O}$ ), (4) Graham, (5) Rose, (6) Collins and Wood, oxidation of Sn by hot  $\text{HNO}_3$  ( $\text{SnO}_2 \cdot 4.2 \text{ H}_2\text{O}$ ), (7) Engel, treatment of sample 6 with  $\text{KOH}$  and  $\text{HNO}_3$ , (8) desiccating sample 6 in a vacuum, (9) drying sample 6 at 100–5° ( $\text{SnO}_2 \cdot 1.1 \text{ H}_2\text{O}$ ), (10) heating sample 6 to redness. From the photograph, the distances of the lines from the center, their angles and their intensities were measured. All the samples, whether stannic acid, amorphous anhyd. oxide or natural oxide, contain a similar central nucleus. Therefore, phys. difference among them is due not to chem. difference but to the manner in which  $\text{H}_2\text{O}$  adheres to the surface of the oxide granules.

S. T.

**The preparation of the cerite earths by means of the difference in solubility of their oxalates in mineral acids.** FR. F. JAINSCIGG. *Edel-Erden u. Erze* 4, 25–6, 47–8 (1923).—A crit. discussion of various procedures for sepg. the metals in cerite. Past methods were tested with a raw material already free from Ce and Yt, but contg. La, Nd and Pr, and slight modifications in some of the procedures were found to be advisable.

C. C. DAVIS

**Synthetic aluminum silicate and its relations to kaolin.** ROBERT SCHWARZ AND ALBERT BRENNER. *Ber.* 56B, 1433–7 (1923).—When dil. neutral aq. solns. of  $\text{AlCl}_3$  and  $\text{Na}_2\text{SiO}_3$  are mixed in the ratios varying from 1:0.75 to 1:1.5 the proportion of  $\text{SiO}_2$  in the ppt. increases until the compn.  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$  is obtained after drying at 110°. This ppt. differs from kaolin in that it is comparatively easily decomposed by concd.  $\text{HCl}$  and loses  $\text{H}_2\text{O}$  at a lower temp. X-ray spectrographs show that 2-day-old and 8-day-old samples were amorphous but that after 8 days a cryst. structure similar to that of kaolin had developed.

D. MACRAE

**Phosphates and arsenates of manganese.** M. AMADORI. *Atti ist. Veneto* 81, 603–17 (1921–2).—A study of equil. in the systems  $\text{MnO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  and  $\text{MnO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$

at 25°, for which diagrams are given with tabulated data. These systems were particularly difficult to investigate because, owing to their tendency to oxidize, neither MnO nor Mn(OH)<sub>2</sub> could be used directly. Resort was had to Mn phosphates and arsenates (prepd. from Na phosphates and arsenates and MnCl<sub>2</sub> or MnSO<sub>4</sub>), which were studied in equil. with varying concns. of aq. H<sub>3</sub>PO<sub>4</sub> and H<sub>3</sub>AsO<sub>4</sub>. From these salts, by hydrolysis, under suitable conditions, other compds. were obtained. The data partly confirm, and partly show to be insufficient, the previous data of Erlenmeyer and Heinrich on Mn phosphates (cf. *Ann.* 190, 191(1878)) and of Debray and of Coriolano on Mn arsenates (cf. *Bull. soc. chim.* 7, 14(1864); 45, 700(1886)). Three new compds. were prepd., the compd. Mn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>PO<sub>4</sub> (I), the compd. Mn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O (II), and the compd. Mn(H<sub>2</sub>AsO<sub>4</sub>)<sub>2</sub>·H<sub>3</sub>AsO<sub>4</sub> (III), the existence of the compd. Mn<sub>3</sub>H<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>·5H<sub>2</sub>O (IV) was established and the previously known compds. MnHPO<sub>4</sub>·3H<sub>2</sub>O (V), Mn(H<sub>2</sub>AsO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (VI) and MnHAsO<sub>4</sub>·H<sub>2</sub>O (VII) were studied. Under the exptl. conditions, the compd. Mn<sub>3</sub>H<sub>2</sub>(AsO<sub>4</sub>)<sub>4</sub> could not be obtained, nor could Mn phosphates or arsenates less acid than those above be prepd. V, prepd. by the method of Erlenmeyer and Heinrich (*loc. cit.*) and by pptn. with EtOH from MnCO<sub>3</sub> in hot satd. aq. H<sub>3</sub>PO<sub>4</sub>, gave intense pink crystals, losing their H<sub>2</sub>O of crystn. below 100°, but their H<sub>2</sub>O of constitution only at high temp. (giving Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>) and decomp. in H<sub>2</sub>O to form unidentified compds. IV, prepd. by making alk. with NaOH and heating a mixt. of aq. NaHPO<sub>4</sub> and MnCl<sub>2</sub> (ratio of 3MnO/P<sub>2</sub>O<sub>5</sub>), gave pink crystals, losing their H<sub>2</sub>O of crystn. at 160°, nearly insol. in H<sub>2</sub>O (0.1 g. per 1000 cc.). Treated with aq. H<sub>3</sub>PO<sub>4</sub> it formed V. II, prepd. by evapg. solns. contg. excess of H<sub>3</sub>PO<sub>4</sub>, gave rose crystals. I, prepd. from solns. contg. a large excess of H<sub>3</sub>PO<sub>4</sub>, gave only minute crystals. I, II and V were hydrolyzed by H<sub>2</sub>O and were stable only in the presence of excess H<sub>3</sub>PO<sub>4</sub>, but IV was stable in H<sub>2</sub>O at 25°. VII, prepd. from solns. contg. Mn and As in the ratio 3MnO/As<sub>2</sub>O<sub>5</sub>, or by pptn. by EtOH of MnCO<sub>3</sub> in satd. H<sub>3</sub>AsO<sub>4</sub>, gave crystals which lost their H<sub>2</sub>O of crystn. below 140°, their H<sub>2</sub>O of constitution at higher temps. and were nearly insol. (0.13 g. per 1000 cc.). An As compd. analogous to IV could not be prepd. by a similar procedure. VI, prepd. from solns. contg. excess H<sub>3</sub>AsO<sub>4</sub>, gave rose crystals. III when prepd. from solns. contg. a large excess of H<sub>3</sub>AsO<sub>4</sub> was microcryst. III and VI were hydrolyzed by H<sub>2</sub>O and were stable only in excess H<sub>2</sub>AsO<sub>4</sub>, but VII was stable in H<sub>2</sub>O at 25°.

C. C. DAVIS

**Permanganates.** III. E. MOLES AND M. CRISP. *Anales soc. españ. fis. quim.* 21, 305-16(1923); cf. C. A. 17, 1762.—The permanganates of Mg, Cd, Cu, Zn, and Fe were prepd. from the corresponding chlorides and AgMnO<sub>4</sub>. All contain H<sub>2</sub>O of crystn. Mg(MnO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cd(MnO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O are somewhat hygroscopic; Cu(MnO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O, Zn(MnO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Ba(MnO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O are deliquescent. The decompn. temps. at which O<sub>2</sub> is liberated are, resp., 150°, 95°, 75°, 95°, 60°. The decompn. temp. for all the known permanganates is a periodic function of the atomic number of the metal. A curve wherein the temps. are plotted against the atomic numbers shows a regular series of peaks and valleys and much resembles curves representing other periodic functions of the elements.

L. E. GILSON

**Ammonium dichromate.** E. MOLES AND F. GONZÁLEZ. *Anales soc. españ. fis. quim.* 21, 204-12(1923).—In order to correct errors existing in the literature certain properties of (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> were detd. with great exactness. d<sub>4</sub><sup>20</sup> 2.1600. Soly., 100 g. satd. soln. at 16° contains 23.88 g.; at 25°, 28.63 g. Heat of soln., -12904 cal. Heat of formation from CrO<sub>3</sub> and NH<sub>4</sub>OH, 23275 cal. when the heat of soln. of CrO<sub>3</sub> in 500 mols. H<sub>2</sub>O is taken as 1190 cal. and the heat of soln. of NH<sub>4</sub>OH in 300 mols. H<sub>2</sub>O is taken as 455 cal. Decompn. begins at 224-6°, once started it will continue at 220°. The residue from decompn. at 220-30° is black Cr<sub>2</sub>O<sub>3</sub> with 6-7% of H<sub>2</sub>O which it tenaciously retains. Heated to 320-30° it loses O and becomes green Cr<sub>2</sub>O<sub>3</sub>.

L. E. G.

**Chlorites of copper and of other metals.** G. R. LEVI AND C. CIPOLLONE. *Gazz. chim. ital.* 53, 200-3(1923).—In continuing earlier work (C. A. 16, 2474, 3271, 3789) the Cu, Cd and Zn salts of HClO<sub>2</sub> were prepd. Molar solns. of CuSO<sub>4</sub> and Ba(ClO<sub>2</sub>)<sub>2</sub> were mixed and after filtration on standing 24 hrs. sepd. about 33% of the Cu as a basic chlorite of variable compn. The filtrate was treated with 9 vols. abs. EtOH and sepd. **cupric chlorite**, Cu(ClO<sub>2</sub>)<sub>2</sub>, as a yellow-brown ppt. that decomposes even in the dry state in 12 days and explodes violently on percussion. Hydrolysis of a soln. of NaClO<sub>2</sub> and CuSO<sub>4</sub> in equiv. amts. by the method used by van der Meulen (*Ber.* 12, 758(1879)) gave **basic cupric chlorite**, Cu(ClO<sub>2</sub>)<sub>2</sub>·3Cu(OH)<sub>2</sub>, which does not explode by percussion. 0.8 mol. concd. KCl soln. added to a N soln. of Cu(ClO<sub>2</sub>)<sub>2</sub> pptd. **potassium cupric chlorite**, Cu(ClO<sub>2</sub>)<sub>2</sub>·2KClO<sub>2</sub>·2H<sub>2</sub>O, which explodes by percussion. **Cupric chloride potassium chlorite**, CuCl<sub>2</sub>·KClO<sub>2</sub>, is obtained by adding insufficient KClO<sub>2</sub> to a concd. soln. of CuCl<sub>2</sub>. **Cupric chloride ammonium chlorite**, CuCl<sub>2</sub>·NH<sub>4</sub>ClO<sub>2</sub>, was obtained similarly.

$\text{BaClO}_2$  soln. +  $\text{Rb}_2\text{CO}_3$  readily gave *rubidium chlorite*,  $\text{RbClO}_2$ , which with  $\text{CuCl}_2$  gave  $\text{CuCl}_2\text{RbClO}_2$ . *Cesium chlorite*,  $\text{CsClO}_2$ , with  $\text{CuCl}_2$  gives  $\text{CuCl}_2\text{CsClO}_2$ .  $\text{BaClO}_2 + \text{CdSO}_4$  gave after filtration *cadmium chlorite*,  $\text{Cd}(\text{ClO}_2)_2 \cdot 2\text{H}_2\text{O}$ , which when pure is stable. *Zinc chlorite*,  $\text{Zn}(\text{ClO}_2)_2 \cdot 2\text{H}_2\text{O}$ , was obtained similarly. Attempts to obtain double chlorites with  $\text{KClO}_2$ , and the Zn and Cd salts failed. E. J. W.

**Chlorites of mercury and of other metals.** G. R. LEVI. *Gazz. chim. ital.* 53, 245-9(1923); cf. preceding abstract.—L. has now extended the study of chlorites of Hg previously mentioned (Bruni and Levi, C. A. 10, 1620).  $\text{Hg}(\text{NO}_3)_2$  is added to a concd. soln. of an alkali or alk. earth chlorite. After about 0.5 equiv. of the  $\text{Hg}(\text{NO}_3)_2$  has been added a permanent red ppt. of *mercuric chlorite*,  $\text{Hg}(\text{ClO}_2)_2$ , appears. This is filtered out and rapidly washed with EtOH. It decomposes without dissolving in warm  $\text{H}_2\text{O}$ ; when dry it explodes violently on percussion. With  $\text{HgNO}_3$  *mercurous chlorite*,  $\text{HgClO}_2$ , is similarly pptd. as a canary-yellow compd. which is also unstable and decomposes on percussion. With excess  $\text{HgNO}_3$  *basic mercurous chlorite hydrate*,  $2\text{HgClO}_2 \cdot \text{HgO} \cdot 5\text{H}_2\text{O}$ , is pptd. as a cream-colored compd. Three types of products were obtained when  $\text{Hg}(\text{ClO}_2)_2$  is treated with insufficient, slight excess and a large excess of  $\text{NH}_4\text{OH}$ , resp. Of these the best defined is *mercuriammonium chlorite*,  $\text{NH}_4(\text{HgOHg})\text{ClO}_2$ , which decomposes, losing Cl compds. Equiv. amts. of  $\text{Ba}(\text{ClO}_2)_2$  and  $\text{NiSO}_4$  (a 2 M soln.) were mixed and filtered. The filtrate was subjected to fractional freezing 5-6 times and its vol. reduced by 0.5 by the sepn. of pure ice. The resulting soln. was fractionally pptd. with abs. EtOH. The 1st and 2nd fractions were basic while the 3rd fraction was pure *nickel chlorite*,  $\text{Ni}(\text{ClO}_2)_2 \cdot 2\text{H}_2\text{O}$ ; it does not explode easily on percussion, but does so on the  $\text{H}_2\text{O}$ -bath. The difficulty in prepn. was due to its great soly. in  $\text{H}_2\text{O}$  and the fact that solns. of  $\text{Ni}(\text{ClO}_2)_2$  easily deposit Ni peroxide.  $\text{Ba}(\text{ClO}_2)_2$  was dissolved in as little  $\text{H}_2\text{O}$  as possible and treated with  $\text{Er}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  and a little  $\text{Ba}(\text{OH})_2$  to make the soln. alk. From this stable soln. (after removing  $\text{BaSO}_4$ ) faintly red *erbium chlorite*,  $\text{Er}(\text{ClO}_2)_2 \cdot 4\text{H}_2\text{O}$ , is pptd. with EtOH. E. J. WITZEMANN

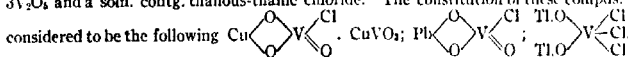
**Univalent thallium in some sulfites.** G. CANNERT. *Gazz. chim. ital.* 53, 182-5(1923).— $\text{H}_2\text{SO}_3$  has the striking property of forming stable complex salts of 2 types:  $[\text{M}^{\text{II}}(\text{SO}_3)_2]\text{M}_2^+$  and  $[\text{M}^{\text{II}}(\text{SO}_3)_2]\text{M}^+$ . C. recently prepd. (C. A. 17, 1600) the corresponding Cu salt:  $[\text{Cu}(\text{SO}_3)_2]\text{Ti}$  in which Cu is bivalent. He has now obtained 6 other salts of the same type by substituting other bivalent metals for Cu: *thallium zinc sulfite*,  $\text{ZnSO}_3 \cdot \text{TiSO}_3$ , pale red; *thallium cadmium sulfite*,  $\text{CdSO}_3 \cdot \text{TiSO}_3$ , red; *thallium ferrous sulfite*,  $\text{FeSO}_3 \cdot \text{TiSO}_3$ , brick-red; *thallium manganous sulfite*,  $\text{MnSO}_3 \cdot \text{TiSO}_3$ , white; *thallium nickel sulfite*,  $\text{NiSO}_3 \cdot \text{TiSO}_3$ , yellow; *thallium cobalt sulfite*,  $\text{CoSO}_3 \cdot \text{TiSO}_3$ , rose-red. The salts were obtained by passing  $\text{SO}_2$  into a  $\text{H}_2\text{O}$  suspension of the bivalent hydroxide until dissolved. The clear soln. was treated with a concd. soln. of  $\text{TiCl}_3$ , which reacts with the excess  $\text{SO}_2$  and ppts. the double salt as microcrystals. E. J. WITZEMANN

**Cobaltous triple nitrites and a sensitive reaction for potassium.** V. CUTTICA. *Gazz. chim. ital.* 53, 185-9(1923).—The triple nitrites constitute one of a small category of inorg. complexes composed of 3 metallic salts of the same acid. Satisfactory knowledge of the factors that det. their formation is not available. Weakly electropositive metals having a low atomic vol. and a weakly electronegative acid are involved (cf. Hansen, C. A. 7, 2142). In a previous paper (C. A. 17, 1928) complex nitrites of Co contg. the quadrivalent group  $\text{Co}(\text{NO}_2)_4$  stable only in the presence of sufficient  $\text{NO}_2$  ions and the cations composing the complex. This group is decomposable into  $\text{Co}(\text{NO}_2)_4^{4-}$  and  $\text{NO}_2^+$  by the action of  $\text{H}_2\text{O}$ . C. has now prepd. and analyzed the following new triple nitrites:  $\text{Co}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot 2\text{KNO}_2$ ;  $\text{Co}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot 2\text{RbNO}_2$ ;  $\text{Co}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot 2\text{NH}_4\text{NO}_2$ ;  $\text{Co}(\text{NO}_2)_2 \cdot \text{Pb}(\text{NO}_2)_2 \cdot 2\text{LiNO}_2$ . They were all obtained as dark green microcrystals by adding a concd. Pb salt soln. to a neutral Co salt soln. and finally an excess of the alkali nitrite. The presence of excess Pb is necessary to prevent the sepn. of  $\text{K}_2$ ,  $\text{Rb}_2$ ,  $\text{TiCo}(\text{NO}_2)_4$ . It is probable that this complex is first formed which

reacts thus:  $\text{K}_2\text{Co}(\text{NO}_2)_4 + \text{K}_2\text{Pb}(\text{NO}_2)_4 \longrightarrow 2\text{KNO}_2 + [\text{Co}(\text{NO}_2)_2]\text{Pb}$ . Because of its insoly. the formation of the latter complex may be used as a qual. test for K, after the elimination of  $\text{NH}_4$  salts, even in the presence of Mg. A cryst. Co salt and  $\text{Pb}(\text{NO}_3)_2$  or  $\text{Pb}(\text{OAc})_2$  are placed on a watch glass and then some drops of a concd. soln. of  $\text{NaNO}_2$ . This is touched with a rod dipped in the liquid to be tested and rubbed against the bottom of the watch glass. In the presence of K in  $\text{H}_2\text{O}$  (1:10000) the green triple salt is pptd. The DeKoninck reagent ( $\text{Na}_2\text{Co}(\text{NO}_2)_4$ ) has about the same sensitivity. E. J. WITZEMANN

**The action of vanadium oxychloride and of nitrosyl chloride on metallic oxides.** V. CUTTICA, A. TARCHI AND P. ALINARI. *Gazz. chim. ital.* 53, 189-94(1923).—On

account of the similarity of V to P it was proposed to synthesize chlorovanadates by the method used by Bassett and Taylor (*C. A.* 6, 461) in the synthesis of chlorophosphates. The behavior of  $\text{POCl}_3$  with metallic oxides is reviewed. The method of Roscoe and Berzelius (*Abegg's Handb. anorg. Chem.* 3, 735(1907)) was used for the prepn. of  $\text{VOCl}_3$ . This consists in calcining  $\text{NH}_4$  metavanadate to obtain  $\text{V}_2\text{O}_5$ , which is reduced to  $\text{V}_2\text{O}_3$  with  $\text{H}_2$ .  $\text{V}_2\text{O}_3$  with dry Cl reacts thus:  $3\text{V}_2\text{O}_3 + 6\text{Cl}_2 \rightarrow \text{V}_2\text{O}_5 + 4\text{VOCl}_3$ . The  $\text{VOCl}_3$  is collected in a flask and redistd. in a current of  $\text{CO}_2$ . The metallic oxides were submitted to the action of  $\text{VOCl}_3$  in sealed tubes at  $150^\circ$  in an oil bath for 3 days. With  $\text{MgO}$  there was obtained a brick-red powder which has no simple rational formula. This product was decompd. by  $\text{H}_2\text{O}$ , giving  $\text{Mg}_2\text{V}_2\text{O}_{17} \cdot 19\text{H}_2\text{O}$ , a previously known hexavanadate. With  $\text{CuO}$  a chlorovanadate  $\text{Cu}(\text{VO}_3)_2 \cdot \text{CuCl}$  was obtained, which with  $\text{H}_2\text{O}$  seps. vanadic acid.  $\text{PbO}$  with  $\text{VOCl}_3$  at  $160^\circ$  gives  $\text{Pb}(\text{VO}_3)_2 \cdot \text{PbCl}_2$ . With  $\text{Ti}_2\text{O}_3$  at room temp.  $\text{Ti}_2\text{O} \cdot \text{VOCl}_3$  is formed, which with  $\text{H}_2\text{O}$  gives a ppt. of  $\text{Ti}_2\text{O} \cdot 3\text{V}_2\text{O}_5$  and a soln. contg. thalious-thallic chloride. The constitution of these compds. is



Of these the 2nd reacts with  $\text{H}_2\text{O}$  giving  $\text{Pb} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{V} \quad \text{OH} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$ . In general the behavior of

$\text{VOCl}_3$  and  $\text{POCl}_3$  is similar. The expts. were then extended to  $\text{NOCl}$ , which was obtained thus:  $\text{HOSO}_2\text{ONO} + \text{NaCl} \rightarrow \text{NOCl} + \text{NaHSO}_4$ . With  $\text{CuO}$  excess  $\text{NOCl}$  gives a red compd. that is rapidly transformed into  $\text{CuCl}_2$  in the air. With  $\text{Cu}_2\text{Cl}_2$ , however,  $\text{NOCl}$  gives  $\text{Cu}_2\text{Cl}_2 \cdot 2\text{NOCl}$ , a black substance. The same compd. is slowly obtained from  $\text{Cu}_2\text{O}$  with  $\text{NOCl}$ . On heating,  $\text{Cu}_2\text{Cl}_2 \cdot 2\text{NOCl}$  decomposes, giving  $2\text{CuCl}_2 + 2\text{NO}$ . With  $\text{Ti}_2\text{O}_3$ ,  $\text{NOCl}$  gave  $\text{TiCl}_3 \cdot 3\text{NOCl}$ , which decomp. slowly *in vacuo*.  $\text{NOCl}$  acts as a chlorinating agent at first as though composed of a mixt. of  $\text{NO} + \text{Cl}$  and resembles  $\text{SO}_2\text{Cl}_2$  in this respect (cf. Spelta, *Gazz. chim. ital.* 34, I, 262(1904)). After this effect is complete  $\text{NOCl}$  adds, giving labile complexes. E. J. WITZEMANN

**Action of hydroxylamine on nitroprussiates.** J. GIRAL. *Anales soc. españ. fis. quim.* 21, 236-44(1923).—Sodium nitroprussiate treated with excess of  $\text{NaOH}$  and then with  $\text{NH}_4\text{OH}$  gives a red ppt. of  $\text{Na}_4\text{Fe}''(\text{CN})_5\text{NO}$ , which when exposed to air oxidizes to yellow  $\text{Na}_4\text{Fe}'''(\text{CN})_5\text{NO}_2 \cdot \text{H}_2\text{O}$ . These compds., their compn. and reactions are discussed at length. The same red ppt. is probably formed with other org. reagents than  $\text{NH}_4\text{OH}$ . L. B. GILSON

**Bismuthamines, a new class of compounds.** A.-CH. VOURNAZOS. *Compt. rend.* 176, 1555-8(1923).—The most characteristic bismuthamines (I) are prepd. by reaction between salts of  $\text{NH}_4$ ,  $\text{RNH}_2$ ,  $\text{R}_2\text{NH}$ , or primary hydrazines, and halogen compds. of Bi, but  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}(\text{NO}_3)_3$ , or complex salts may be used; org. salts usually give amorphous amines. When Bi and N derivs. of the same acid react, the product is of the type  $\text{BiCl}_3 \cdot \text{RNH}_2 \cdot \text{HCl}$ ; with e. g.,  $\text{BiBr}_3$  and  $\text{RNH}_2$ ,  $\text{HNO}_3$ , the product is  $\text{BiBr}_3 \cdot \text{RNH}_2 \cdot \text{HNO}_3$ , but the reaction  $\text{Bi}(\text{NO}_3)_3 + 3\text{RNH}_2 \cdot \text{HBr}$  gives also  $\text{BiBr}_3 \cdot \text{RNH}_2 \cdot \text{HNO}_3$ , and  $2\text{RNH}_2 \cdot \text{HNO}_3$ . Compds. of  $\text{NH}_4$  are more complex, salts of unstable acids of the type H. ( $\text{BiBr}_4$ ) being formed; salts such as  $\text{NH}_4 \cdot (\text{BiBr}_4\text{OAc})$  no longer give the usual Bi reactions. These syntheses are best carried out in glacial  $\text{AcOH}$ ; the procedure is to add the Bi salt as a dry powder or in hot  $\text{AcOH}$  soln. to the salt of the N compd.; in hot  $\text{AcOH}$ , the product is filtered off usually in cryst. form.  $\text{H}_2\text{O}$  or  $\text{EtOH}$  decomp. I, which are decompd. also on heating above  $400^\circ$ . Ten examples are briefly described. A. R. ALBRIGHT

**Derivatives of hexachloroantimonic acid.** A. GUTHIER AND W. HAUSSMANN. *Z. anorg. allgem. Chem.* 128, 153-68(1923).—The salts of  $\text{HSbCl}_6$  with the following organic bases were prepd., and their crystal form and habit, soly. in alc. and  $\text{HCl}$ , and behavior with water were detd.: methyl-, dimethyl-, trimethyl-, tetramethyl-, ethyl-, diethyl-, triethyl-, tetraethyl-, propyl-, isopropyl-, dipropyl-, tripropyl-, butyl-, isobutyl-, diisobutyl-, allyl-, isoamyl-, benzyl-, and dibenzylethylammonium, ethylene-diamine (formula of salt  $[\text{C}_2\text{H}_4 \cdot \text{N}_2\text{H}_5]_2(\text{SbCl}_6)$ ), suggested structural formula  $(\text{SbCl}_6)_2$

$\text{H} \begin{array}{c} \text{NH}_2 - \text{CH}_2 \\ | \\ \text{NH}_2 - \text{CH}_2 \end{array}$ ;  $\alpha$ -picoline; collidine and piperidine. The method of prepn., etc., was similar to that of the hexachlorobismuthates (cf. preceding abstract). R. S. M.

**Derivatives of hexachlorostannic acid.** A. GUTHIER, G. KUNZE AND E. GÜHRING. *Z. anorg. allgem. Chem.* 128, 169-78(1923).—The prepn. and properties of salts of  $\text{H}_2\text{SnCl}_6$  with organic bases are described. The salts are mostly colorless, well crystd., mostly easily sol. in  $\text{HCl}$ , water, and alc., and slowly hydrolyzed by water. Crystal

form and habit are given, in most cases for the first time. Most of the compds. are new. The following salts were prepd.: methyl-, dimethyl-, trimethyl-, tetramethyl-, ethyl-, diethyl-, triethyl-, tetraethyl-, propyl-, isopropyl-, dipropyl-, tripropyl-, butyl-, isobutyl-, diisobutyl-, triisobutyl-, allyl-, and isoamylammonium, ethylene and propylene-diamine, aniline, pyridine, collidine and quinoline. R. S. MULLIKEN

**Studies on chlorobismuthates.** A. GUTHRIE AND MANFRED MÜLLER. *Z. anorg. allgem. Chem.* 128, 137-52(1923).—On account of their comparative stability the substituted ammonium salts of the chlorobismuthic acids were studied. Since the solvent often has a detg. effect on the compn. of the product, the compds. here prepd. were all crystd. from concd. aq. HCl. All the compds. below were prepd. by adding 3 mols. of the org. base to 1 mol. of BiCl<sub>3</sub> in HCl soln., and recrystallizing from HCl. The products are all colorless and well crystd., and are mostly unstable in air and decompd. by water to BiOCl. The reaction product is usually, as expected, a salt of H<sub>2</sub>BiCl<sub>4</sub>, but in some cases is of the type R<sub>2</sub>BiCl<sub>3</sub> or R<sub>3</sub>BiCl<sub>2</sub>. G. and M. formulate the 3 types as follows: (A), hexachlorobismuthates, R<sub>3</sub>+ $\left[ \begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{Cl} \rightarrow \text{Bi} \leftarrow \text{Cl} \\ \diagdown \quad \diagup \\ \text{Cl} \end{array} \right]^-$ ; (B),  $\mu$ -dichlorooctachloro-

dibismuthates, R<sub>4</sub>+ $\left[ \begin{array}{c} \text{Cl} \quad \text{Cl} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{Cl} \rightarrow \text{Bi} \leftarrow \text{Cl} \quad \text{Cl} \rightarrow \text{Bi} \leftarrow \text{Cl} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{Cl} \quad \text{Cl} \end{array} \right]^-$ ; (C),  $\mu$ -trichlorohexachlorodibis-

muthates, R<sub>4</sub>+ $\left[ \begin{array}{c} \text{Cl} \quad \text{Cl} \quad \text{Cl} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{Cl} \rightarrow \text{Bi} \leftarrow \text{Cl} \quad \text{Cl} \rightarrow \text{Bi} \leftarrow \text{Cl} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{Cl} \quad \text{Cl} \quad \text{Cl} \end{array} \right]^-$ . A study of the structure by means of chem.

reactions was not possible, on account of the instability of the compds. in aq. solns. Salts of the following org. bases were prepd., and the crystal form and habit detd. in most cases (all but the first 3 are new compds.): type (B), salts of dimethyl- and diethylaniline; type (C), the methyl-, tetramethyl-, triethyl-, tetraethyl-, propyl-, tripropyl-, butyl-, isobutyl-, and isoamylammonium salts: type (A), dimethyl-, trimethyl-, methyl-, monoethyl-, isopropyl-, dipropyl-, and allylammonium salts and salts of monoethyl-, diethyl-, and isoamylaniline, guanidine, pyridine,  $\alpha$ - and  $\beta$ -picoline, lutidine, collidine, quinoline, and isoquinoline. R. S. MULLIKEN

$\beta$ -Cobaltous iodide (BIRK, BULTZ) 2. Hydrous oxides. V. Hydrous cupric oxide (WEISER) 2.

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

**Avoidance of simultaneous equations.** A. FAIRBOURNE. *Analyst* 48, 263-4 (1923).—Indirect analyses such as the detn. of Cl in a mixt of KCl and NaCl when the % of KCl and NaCl is desired are often solved algebraically by the use of simultaneous equations. This is unnecessary. Suppose the compd. A contains 12% of a given constituent when pure and the compd. B contains 83% of the same constituent. To find the ratio of A to B in a mixt. contg. say 47% of the common constituent arrange the values thus:

$$\begin{array}{rcl} A = 12 & \nearrow & 36 \\ B = 83 & \searrow & 35 \end{array}$$
 and subtract along the diagonals, taking the smaller no. from the larger. In this case there will be 36 parts of A mixed with 35 of B by wt. or 36/71 of the entire wt. will give the wt. of A. W. T. H.

**A source of trouble in electrometric measurements of hydrogen-ion concentration.** W. T. BOVIE AND W. S. HUGHES. *J. Am. Chem. Soc.* 45, 1904-5(1923).—In using a Hg/Hg<sub>2</sub>Cl<sub>2</sub> half cell for electrometric measurements some HgCl<sub>2</sub> formed at the electrode is likely to work back into the soln. and poison the H<sub>2</sub> electrode. This difficulty has been overcome by sepg. the solns. by a very thin glass bulb. W. T. HALL

**Estimation of arsenic by the electrolytic method.** G. W. MONIER-WILLIAMS. *Analyst* 48, 262-3(1923); cf. C. A. 17, 1906.—The use of fresh Pb foil prevents low results when Fe or phosphate is present. To test CaH<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub> for As, take 3.5 g. of powder, 20 cc. of water and 5 cc. of concd. H<sub>2</sub>SO<sub>4</sub>. Add 2.5 g. of whole milk powder and also 2 cc. of amyl alc. In the porous pot which serves as electrolytic cell, dil. with enough water to cover the electrodes. Strips of Pb foil at least 0.5 in. wide can lead to the elec-

trodes and a vertical strip of lead foil can replace the horizontal disk for viscous electrolytes.

W. T. H.

**The general principles of molybdomanganimetry.** G. FONTES AND L. THIVOLLE. *Bull. soc. chim.* 33, 835-40(1923); cf. *C. A.* 17, 1199.—Molybdomanganimetry is the name given to the series of reactions which involve the formation of molybdenum blue by the action of a reducing agent upon a soln. of  $\text{Na}_2\text{MoO}_4$  and the titration of the molybdenum blue with standard  $\text{KMnO}_4$  soln. As reducing agents  $\text{Cu}_2\text{O}$ ,  $\text{Fe}^{++}$ ,  $\text{Sn}^{++}$ ,  $\text{Na}_2\text{S}_2\text{O}_4$  or metals such as Cu, Fe, Zn and Mg may be used. The usual reduction is to quadrivalent Mo and treatment with  $\text{KMnO}_4$  oxidizes Mo back to the 6-valent condition. To prep. the Mo reagent, dissolve 40 g. of  $\text{NH}_4$  molybdate in 60 cc. of  $\text{NaOH}$  soln. (d. 1.36) diluted with 100 cc. of water. Boil till  $\text{NH}_3$  is all expelled, add water to make 200 cc. and also add 200 cc. of  $\text{H}_3\text{PO}_4$  (d. 1.38). Boil the mixt. 15 mins. and dilute to 1000 cc. Prep. a soln. of  $\text{KMnO}_4$  by dissolving 8 g. of  $\text{KMnO}_4$  in 100 cc. of  $\text{H}_2\text{O}$  and dil. this 100-fold for the titrations. For standardizing the  $\text{KMnO}_4$  soln., Mohr's salt is useful. Dissolve 1.4 g. in water, add 1 cc. of 60° B $\phi$ .  $\text{H}_3\text{PO}_4$  and dil. to 1000 cc. The  $\text{H}_3\text{PO}_4$  makes the  $\text{Fe}^{++}$  soln. more stable.

W. T. H.

**The analytical utilization of the molybdenum blue reaction.** F. FEIGL. *Chem.-Ztg.* 47, 561(1923).—F. has used the reaction for 3 yrs. in his classes in testing for Sn, Sb, As and Cu. Molybdenum in the presence of phosphoric acid is reduced to the valence of 3 and no lower. Colorimetric methods can be worked out for the estn. of As, Cu and Sn and the blue can be shaken out with amyl alc. for a better comparison. The use of  $\text{HNO}_3$  in the Sn detn. is less satisfactory than  $\text{HCl}$  because with the latter there is less danger of oxidation before the Mo compd. has been added.

W. T. H.

**The microdetermination of copper by molybdomanganimetry.** G. FONTES AND L. THIVOLLE. *Bull. soc. chim.* 33, 840-44(1923).—By this method 0.1 mg. Cu or less can be detd. Three methods are proposed for getting the Cu in a reduced condition so that it will react with  $\text{Na}_2\text{MoO}_4$  reagent.  $\text{Cu}_2\text{O}$  can be pptd. by boiling the alk. soln. with glycerol and an excess of glucose and the ppt. can be treated with the Mo reagent or the Cu may be deposited electrolytically in a vol. of about 5 cc. in a narrow tube. To the soln. add 3 drops of concd.  $\text{H}_2\text{SO}_4$  and an equal vol. of concd.  $\text{HNO}_3$ , add water to cover the electrodes and electrolyze. It is well to have a stopcock at the bottom of the electrolyzing tube so that at the end of the electrolysis the soln. may be withdrawn while the electrodes are being washed. When the electrolysis is finished, plunge the washed cathode into the Mo reagent and titrate the Mo blue with dil.  $\text{KMnO}_4$ . Another method consists in producing Cu by igniting the cupferron ppt. in  $\text{H}_2$ .

W. T. H.

**Microdetermination of iron by molybdomanganimetry.** G. FONTES AND L. THIVOLLE. *Bull. soc. chim.* 33, 844-9(1923).—Small quantities of Fe can be detd. after forming  $\text{Fe}^{++}$  or after getting metallic Fe.  $\text{Fe}^{+++}$  can be reduced to  $\text{Fe}^{++}$  by means of clean Cu wire suspended in the dil. Fe soln. contg. 1-2 cc. of  $\text{H}_3\text{PO}_4$  of 40° B $\phi$ . Boil 10 min. in an Erlenmeyer flask, cool, filter and treat the filtrate with 5 cc. of the Mo reagent. Another method consists in pptg. Fe with  $\alpha$ -nitroso- $\beta$ -naphthol in very dil.  $\text{H}_2\text{SO}_4$  soln. Ignite the ppt. in  $\text{H}_2$ , stopping as soon as the ppt. begins to condense. In this way finely divided Fe is obtained which is not pyrophoric. As sensitive reagent prep. a soln. by dissolving 40 g.  $\text{NH}_4$  molybdate and 10 g. pure  $\text{NaOH}$  in 100 cc. of water. Boil off  $\text{NH}_3$ , add 250 cc. of  $\text{H}_3\text{PO}_4$  (d. 1.30), and 0.5 g.  $\text{CuCO}_3$ . Boil 15 min. and dil. to 1 liter.

W. T. H.

**Chronometric determination of iodine in soluble iodides.** E. RIEGLER. *Bull. soc. chim. Romania* 5, 3-5(1923); cf. *C. A.* 17, 1040.—Ten cc. of a soln. contg. 0.2-3.0 mg. of  $\text{I}^-$  are mixed with 5 drops of 2%  $\text{NaNO}_2$  soln., 5 drops of 1% sol. starch soln., and 5 drops of 2%  $\text{H}_2\text{SO}_4$ . The time required to decolorize the soln. after the addition of 2 cc. of 2% ethyl acetoacetate soln. is taken with a stopwatch; 5 sec. is required at 18° for each 0.1 mg. of  $\text{I}^-$  present.

W. T. HALL

**The titration of silver ions and chloride ions in the presence of protective colloids.** W. D. TRADWELL, S. JANETT AND M. BLUMENTHAL. *Helvetica Chim. Acta* 6, 513-8 (1923).—The presence of a protective colloid such as gelatin increases the soly. of  $\text{AgCl}$  but has little effect upon the electrometric titration of Ag with  $\text{NaCl}$  soln.; the absence of a ppt. at the end point is favorable rather than otherwise. On the other hand there are some medicinal Ag preps. which do not give the entire Ag content when titrated with  $\text{NaCl}$  soln. electrometrically. In such cases the total Ag can be detd. by destroying the org. matter by fusing with  $\text{Na}_2\text{O}_2$  or by titrating electrometrically with  $\text{Na}_2\text{S}$ . The Ag ion and total Ag content of a number of pharmaceutical products were detd.

W. T. H.

**Note on the determination of phosphorus in bronze.** N. WELWART. *Oesterr.*



*Chem.-Ztg.* 26, 93-4(1923).—Even when 20 times as much Sn as P is present, the meta-stannic acid residue obtained by treating the bronze with  $\text{HNO}_3$  does not contain all of the P.

W. T. HALL

**The estimation of tin in tungsten. Modification of Powell's method.** O. F. LUBATTI. *J. Chem. Soc.* 123, 1409-11(1923).—Fuse 10 g. of 200-mesh ore for 10 min. in a silica dish with 7 g. of  $\text{K}_2\text{S}_2\text{O}_7$ . Ext. the melt with 200 cc. of 5% tartaric acid soln., sat. with  $\text{H}_2\text{S}$  and filter. Wash the residue 3 times with hot tartaric acid soln. Ignite the residue, contg. all the Sn, in a porcelain crucible. Meanwhile prep. another crucible with ZnO sprinkled on the bottom and on top of this 2 g. of Zn filings. Mix the ash in the first crucible with ZnO and transfer to the second crucible, using about 0.5 g. ZnO in all. Cover the crucible with an inverted lid and heat to about  $1000^\circ$ . A suitable furnace can be made by cutting off the bottom of a Battersea crucible and inserting a quartz triangle to hold the smaller crucible. Cover the Battersea crucible with a scorifier having a hole in the middle. Heat with a No. 4 Méker burner. After 10 minutes heating, whereby  $\text{SnO}_2$  is reduced to Sn, cool and treat with a mixt. of 50 cc. concd.  $\text{HCl}$ , 1 g.  $\text{KMnO}_4$  and 10 g.  $\text{NaCl}$ . Boil 15 min. and dil. to about 175 cc. Add 10 g. of Sb in fragments and cover with a funnel contg. a few pieces of pure marble. Boil 20 mins. after the color of  $\text{FeCl}_3$  has disappeared. Add a little marble to the soln., cool rapidly and titrate the  $\text{Sn}^{++}$  with standard  $\text{I}_2$  soln. using starch as indicator.

W. T. HALL

**A new gravimetric method for the determination of iron and for its separation from manganese by a mercury salt.** B. SOLAJA. *Chem.-Ztg.* 47, 557(1923).—A preliminary announcement of the successful detn. of  $\text{Fe}^{+++}$  by the use of  $\text{HgNH}_2\text{Cl}$  instead of  $\text{NH}_4\text{OH}$  as a precipitant. Values are given for both Mn and Fe in artificial mixts. but the exact details of the method are not stated.

W. T. H.

**The determination of metal sulfides by heating in hydrogen sulfide.** L. MOSER AND E. NEUSSER. *Chem.-Ztg.* 47, 541-3, 581-2(1923).—A ppt. of  $\text{PbS}$  can be weighed after heating for 1 hr. at  $300-550^\circ$  in a stream of  $\text{H}_2\text{S}$ , and cooling in the same atm. Similarly,  $\text{Pb}(\text{OH})_2$ ,  $\text{PbO}$ ,  $\text{PbCO}_3$ ,  $\text{PbSO}_4$  and  $\text{PbCl}_2$  can be converted quantitatively to  $\text{PbS}$  by heating in  $\text{H}_2\text{S}$ . A ppt. of  $\text{Bi}_2\text{S}_3$  can be weighed after heating in  $\text{H}_2\text{S}$  for 1 hr. at  $270^\circ$ . Other sulfides mentioned in the literature are probably mixts. of  $\text{Bi}_2\text{S}_3$  and Bi.  $\text{TiS}_3$  can be weighed after heating 45 mins. in a stream of pure  $\text{H}_2\text{S}$ . To ppt.  $\text{TiS}_3$  introduce  $\text{H}_2\text{S}$  into the neutral or dil.  $\text{AcOH}$  soln. and finally add a slight excess of  $\text{NH}_4\text{OH}$ .  $\text{Sb}_2\text{S}_3$  can be weighed after heating in  $\text{H}_2\text{S}$  at  $270^\circ$ . Similar expts. with W, Mo, Ni, Co and Sn did not lead to satisfactory results.

W. T. HALL

**The estimation of lead in acid calcium phosphate (cream powder).** J. MILLER. *Analyst* 48, 263(1923).—If starch is present ignite 10 g. in a silica dish. Digest with 20 cc. of hot concd.  $\text{HCl}$  and dil. with 50 cc. of water. Filter, wash with hot water and add 0.6 cc. of Fehling soln. Add  $\text{NH}_4\text{OH}$  until a slight ppt. forms and dissolve this by adding 2 cc. of  $\text{HCl}$ . Sat. with  $\text{H}_2\text{S}$ , filter and ignite the ppt. in a quartz crucible. Digest the oxide residue with 10 cc. of 1.5  $N$   $\text{HNO}_3$ . Dil. to about 50 cc., add  $\text{NH}_4\text{OH}$  until slightly ammoniacal and make up to exactly 100 cc. Add 1 cc. of 10%  $\text{KCN}$  soln. and 2 drops of  $\text{Na}_2\text{S}$  soln. Compare the color with that obtained with 0.6 cc. of Fehling soln. treated with  $\text{HNO}_3$ , etc., as above.

W. T. H.

**The determination of barium as oxalate.** B. N. ANGELSCU. *Bul. soc. chim. Romania* 5, 12-15(1923).—To the concd. aq. soln. contg. about 0.25 g. Ba, add 3 vols. alc. and ppt. with a slight excess of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  soln. Let stand on the water bath for 10 min. to make the ppt. cryst. After an hr. filter, wash with 75% alc., dry at  $70^\circ$  for about 2 hrs. and weigh as  $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . Allow 2 mg. for soly. of ppt.

W. T. HALL

**Further notes on the estimation of potassium by the perchlorate and cobaltinitrite methods and on the removal of sulfates.** R. L. MORRIS. *Analyst* 48, 250-60(1923).—Test analyses show that the  $\text{HClO}_4$  method is accurate in the absence of sulfate and ammonium salts. In the presence of alk. earths it is sometimes necessary, when phosphate is present, to redissolve the first  $\text{KClO}_4$  ppt. and repeat the pptn. To remove sulfate add 10%  $\text{BaCl}_2$  in slight excess to the soln., not more than 80 cc. in vol. and contg. not more than enough  $\text{SO}_4$  to make 1.2 g. of  $\text{BaSO}_4$  and contg.  $1/4$  its vol. of concd.  $\text{HCl}$ . Ignite the  $\text{BaSO}_4$  ppt. and boil it 10 mins. with 50 cc. of water contg. a few drops of  $\text{HCl}$ . Add the soln. thus obtained to the original filtrate from the  $\text{BaSO}_4$ . Wash the  $\text{KClO}_4$  ppt. first with 97% alc. and then with alc. contg. 0.2%  $\text{KClO}_4$ , using about 35 cc. of wash liquid in all. From this filtrate alc. can be recovered if enough pure  $\text{NaOH}$  is added to make the soln. alk. Explosions are probably due to the formation of ethyl perchlorate, which ought not to form if the alc. is alk. The cobaltinitrite method of Adie and Wood gives good results and the same is true of the modification of Druschel.

In the former method the analysis is based upon the titration of  $\text{NO}_3^-$  in the pptn. of  $\text{K}_2\text{NaCo}(\text{NO}_3)_6 \cdot \text{H}_2\text{O}$  after the removal of the Co but the latter depends upon the titration in presence of Co so that the factor is  $1/2$ , as large in the latter case; 1 cc. 0.1 *N*  $\text{KMnO}_4 = 0.000785$  g.  $\text{K}_2\text{O}$ . The modified procedure is as follows: To the neutral soln. contg. Na and K but no  $\text{NH}_4$  add  $\text{AcOH}$  and evap. to 10 cc. Add 10–15 cc. of reagent prep'd. by mixing equal vols. of solns. A and B; soln. A, 113 g.  $\text{Co}(\text{OAc})_2$  crystals or 130 g.  $\text{Co}(\text{NO}_3)_2$ , 100 cc.  $\text{AcOH}$  and water to make 500 cc.; soln. B, 220 g.  $\text{NaNO}_2$  and water to make 500 cc. Warm gently till effervescence ceases and evap. to a paste. Cool and ext. the sol. Na salts with cold water or 10%  $\text{AcOH}$ . After the ppt. has settled, decant through a Gooch crucible and wash the ppt. with 15%  $\text{NaCl}$ . Heat the moist ppt. with water and an excess of standard  $\text{KMnO}_4$ , boiling for 10 mins. Add sulfuric acid, boil 10 mins. and add more than enough of standard oxalic acid to react with the excess  $\text{KMnO}_4$ . Finally titrate the excess oxalate with standard  $\text{KMnO}_4$ . W. T. H.

**A method for determining zinc and lead in materials containing large amounts of carbon.** W. KAHLBAUM. *Eng. Mining J. Press* 116, 110–11 (1923). To destroy carbonaceous matter heat in a bomb similar to Parr's calorimeter except that it should be made of mild steel. Heat 0.5 g. of sample with 5–10 g. of pure  $\text{Na}_2\text{O}_2$ . As soon as the reaction starts remove the blast lamp and cool in running water before the upper part of the bomb gets too hot. Leach with water and dissolve the insol. hydroxides in dil. acid. To det. Zn, add 5 g.  $\text{NH}_4\text{Cl}$ , 20 cc.  $\text{NH}_4\text{OH}$  and a little  $\text{H}_2\text{O}_2$ . Filter and titrate the filtrate with  $\text{K}_2\text{Fe}(\text{CN})_6$  in the usual way. To det. Pb, acidify with  $\text{HNO}_3$ , add concd.  $\text{H}_2\text{SO}_4$  and continue in the usual way with the molybdate method or if the Pb content is low it can be det'd. electrolytically. W. T. H.

**A method of analysis for alkali phosphotungstates.** R. MIELLET. *Helvetica Chim. Acta* 6, 656–61 (1923).—Heat the sample to const. wt. in a Pt crucible; loss in wt. is  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}$  and  $\text{NH}_3$ . Fuse with 4–5 times as much  $\text{Na}_2\text{CO}_3$ . Dissolve the melt in water, add twice as much  $\text{NH}_4\text{Cl}$  as was used of  $\text{Na}_2\text{CO}_3$  and ppt.  $\text{MgNH}_4\text{P}_2\text{O}_7$  in the usual way. Dissolve the ppt. in acid and repeat the pptn. To det.  $\text{WO}_3$  in another portion, use as reagent, a soln. contg. 20 g. quinoline and 50 g.  $\text{AcOH}$  per liter. Add the reagent at 60° in slight excess and wash with reagent diluted with 3 vols. of water. Ignite and weigh  $\text{WO}_3$  and some  $\text{P}_2\text{O}_5$ . Det.  $\text{P}_2\text{O}_5$  as outlined above and deduct the corresponding wt. from that of the impure  $\text{WO}_3$ . Alkalies are easiest to det. by difference. W. T. H.

**The determination of sulfur and some of its compounds.** J. M. TAYLOR. *J. Soc. Chem. Ind.* 42, 294–7T (1923).—T. recommends adding fairly dil.  $\text{BaCl}_2$  soln. and the fairly dil.  $\text{SO}_4^{--}$  soln. both at the same time into dil.  $\text{HCl}$ . In this way both ions are dil. when pptn. takes place but the total vol. of soln. is kept reasonably small. To det. S in native S digest the sample with  $\text{Br}$  aq. Add  $\text{BaCl}_2$ , neutralize with  $\text{NH}_4\text{OH}$  and add 0.5 cc. concd.  $\text{HCl}$ . Filter and weigh the  $\text{BaSO}_4$ . To det. S in  $\text{S}_2\text{Cl}_2$  proceed similarly, weighing out the sample in an oleum bulb. To det. S in leucotrope, fuse 0.5 g. with 15 g.  $\text{Na}_2\text{O}_2$  in an Ni crucible, ext. with water, boil to decompose excess peroxide, make acid with  $\text{HCl}$  and ppt. with  $\text{BaCl}_2$ . To analyze  $\text{SO}_2\text{HCl}$  weigh out 1.5–2 g. in an oleum bulb and titrate the total acidity with  $\text{NaOH}$  and methyl orange as indicator and then titrate Cl by the Mohr method. To analyze  $\text{SOCl}_2$  det. the total acidity with methyl orange as indicator. Distil off free  $\text{SO}_2$  from another sample and catch the distillate in water contg.  $\text{H}_2\text{O}_2$ . Since some  $\text{SOCl}_2$  distills as well as the free  $\text{SO}_2$ , titrate the acidity and also the chlorine. To analyze  $\text{SO}_2\text{Cl}_2$  treat the weighed sample with boiled water, det. free  $\text{SO}_2$  and ppt.  $\text{BaSO}_4$ . Estimate  $\text{S}_2\text{Cl}_2$  by color when  $\text{Cl}_2$  is introduced. W. T. H.

**The influence of alkali on the titration of certain metals with ferrocyanide.** II. W. D. TREADWELL AND D. CHERVET. *Helvetica Chim. Acta* 6, 550–9 (1923); cf. C. A. 17, 38.—When Zn is titrated electrometrically with  $\text{Na}_4\text{Fe}(\text{CN})_6$  the end point corresponds to the formation of  $\text{Zn}_2\text{Fe}(\text{CN})_6$  but if a little  $\text{KCl}$  and  $\text{HCl}$  is added,  $\text{ZnK}_2[\text{Fe}(\text{CN})_6]_2$  is obtained. With Ni, the ppt. is  $\text{Ni}_2\text{Fe}(\text{CN})_6$  when Li ferrocyanide is the reagent,  $\text{Ni}_2\text{Na}_2[\text{Fe}(\text{CN})_6]_2$  when the Na salt is used and  $\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]_2$  with the K salt. The results with Co are about the same. When Cs ferrocyanide is used in the titration,  $\text{Cs}_2\text{Co}[\text{Fe}(\text{CN})_6]_2$  is obtained. When a Mn soln. is titrated  $\text{Mn}_2\text{Fe}(\text{CN})_6$  is the ppt. with Li or Na ferrocyanide but  $\text{K}_2\text{MnFe}(\text{CN})_6$  is formed with the K salt. In titrating  $\text{Ag}^+$ ,  $\text{Ag}_2\text{Fe}(\text{CN})_6$  is obtained with Li, Na and K ferrocyanides but  $\text{Ag}_2\text{CsFe}(\text{CN})_6$  is formed with the Cs salt. With the rare earths ppts. of  $\text{LaCs}_2\text{Fe}(\text{CN})_6$  and  $\text{Ce}_2\text{Fe}(\text{CN})_6$  were obtained. W. T. HALL.

**Theoretical discussion of the results of the above paper.** W. D. TREADWELL. *Helvetica Chim. Acta* 6, 559–61 (1923).—The penetration of alkali ions into the above ppts. which are to be regarded as solid solns. is similar to the effect of permittite as a water softener. A study of the heats of hydration of the ions indicates that differences

in the free energy of hydration are to be regarded as the driving forces causing the adsorption of alkali ion. The heat of hydration varies in the alkali group from Li to Cs and is least with Cs which approaches the corresponding values of the heavy metals.

W. T. HALL

**A method for determining sodium.** A. BLANCHETIERE. *Bull. soc. chim.* 33, 807-18(1923).—In biological work Na is usually detd. as pyroantimonate but the results are not always satisfactory. Under suitable conditions it is possible to form a ppt. of the acetates of U, Mg and Na of the following compn.— $3\text{UO}_2(\text{AcO})_2$ ,  $\text{Mg}(\text{AcO})_2$ ,  $\text{NaAcO} \cdot 9\text{H}_2\text{O}$ . As reagent prep. a soln. of 100 g.  $\text{UO}_2(\text{AcO})_2$ , 60 g.  $\text{AcOH}$  and enough water to make 1000 cc., also a soln. of 333 g.  $\text{Mg}(\text{AcO})_2$ , 60 g.  $\text{AcOH}$  and water to make 1000 cc. Mix equal vols. of the 2 solns. To the Na soln. of small vol., add 10 vols. of the mixt. Stir, wait 30 min. and filter through a Gooch crucible that has been wet with the reagent. Filter, using gentle suction so that 1-2 drops per sec. run through the crucible, wash 3 times with dil. reagent, and 3 times with 95% alc. Dry at  $110^\circ$  and weigh.

W. T. H.

**A method for the rapid titration of dark solutions.** F. KRYZ. *Oesterr. Chem. Ztg.* 26, 94(1923).—The acidity of molasses and similar dark colored solns. can be detd. by titration in a vessel of which the opposite sides are parallel and not very far apart. The soln. is diluted until it is fairly transparent, indicator is added and the change of color watched by looking through the soln. toward a window.

W. T. H.

**The estimation of simple soluble cyanogen compounds, making use of the principle of aeration.** J. H. ROE. *J. Am. Chem. Soc.* 45, 1878-9(1923).—To remove HCN by boiling is objectionable because some  $\text{HCOONH}_4$  is formed in the distg. flask by hydrolysis. It is safer to remove HCN by simply passing 350-500 l. of air through the soln. Dissociable cyanides can be detd. by adding an excess of tartaric acid, passing air through the soln., absorbing the HCN in 5% NaOH soln. and titrating with  $\text{AgNO}_3$ . For  $\text{Hg}(\text{CN})_2$  a preliminary treatment with HCl and  $\text{SnCl}_2$  is necessary.

W. T. HALL

**The determination of carbon monoxide in air.** M. NICLOUX. *Bull. soc. chim.* 33, 818-22(1923).—The most satisfactory test for CO is the formation of characteristic absorption bands with the hemoglobin of blood. To det. the quantity it is merely necessary to det. how much air is required to make the absorption bands visible. The fresh beef blood should be treated with 0.1 vol. of alc. added very slowly to prevent fermentation and clotting. Remove the  $\text{O}_2$  from the air by treatment with a soln. of 20 g.  $\text{Na}_2\text{S}_2\text{O}_4$ , 20 cc. of NaOH soln.,  $36^\circ \text{Bé.}$  and 80-100 cc. of water. Mix 0.2-0.3 cc. of the blood with 18 cc. of water and 2 cc. of ammoniacal Na hyposulfite soln. (60 mg.  $\text{Na}_2\text{S}_2\text{O}_4$  and 20 cc. of 0.3 N  $\text{NH}_4\text{OH}$ ). Pass the air at the rate of 600 cc. per hr.

W. T. H.

**New volumetric method for elementary analysis.** L. HACKSPILL and G. HEECK-EREN. *Compt. rend.* 177, 59-60(1923).—This method provides for the detn. of C, H and N in a single sample of an org. substance. By combustion with CuO at  $900^\circ$ , a mixt. of  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$  is obtained. By cooling with  $\text{CO}_2$  snow and acetone, the moisture is all condensed to water at  $-80^\circ$ . The  $\text{CO}_2$  is detd. by the reduction of vol. after absorption in alkali and the vol. of residual  $\text{N}_2$  detd. The condensed  $\text{H}_2\text{O}$  is allowed to react with  $\text{CaH}_2$  and the vol. of  $\text{H}_2$  detd.

W. T. HALL

**New method for the volumetric determination of acetone.** A. IONESCU, E. SPRI-RESCU and D. POPESCU. *Bul. soc. chim. Romania* 5, 15-21(1923).—The method depends upon pptg. the acetone as  $\text{Hg}_2\text{SO}_4 \cdot 3\text{HgO} \cdot 4\text{CH}_3\text{COCH}_3$ , dissolving the ppt. and titrating the Hg with NaCl soln. using  $\text{Na}_2\text{NO}(\text{CN})_2$  as indicator. Place 1-10 cc. of the acetone soln. in a 200-cc. Erlenmeyer flask, add 10 cc. of 18 N  $\text{H}_2\text{SO}_4$ , 10 cc. of  $\text{Hg}_2\text{SO}_4$  reagent (0.5 N in  $\text{HgSO}_4$ , 2.5 N in  $\text{H}_2\text{SO}_4$ ) and 100 cc. water. Boil 20 min. to effect pptn. of the acetone. Cool, filter and wash several times with 200 cc. water. Open up the filter and transfer the ppt. to an Erlenmeyer flask. Add 25 cc. of a mixt. of 1 vol. concd.  $\text{HNO}_3$  and 2 vols. concd.  $\text{H}_2\text{SO}_4$  and heat gently to dissolve the ppt. Remove nitrous compds. by adding a few drops of 10%  $\text{KMnO}_4$ , pour into a beaker contg. 100 cc. of water, add 12 drops of 10%  $\text{Na}_2\text{NO}(\text{CN})_2$  soln. and titrate with 0.1 N NaCl until the turbidity disappears. Standardize the NaCl soln. against 5% acetone soln. Seven expts. with 0.5 to 10 cc. of the acetone soln. gave values agreeing within 5% of the acetone content.

W. T. HALL

Cobaltous triple nitrites and a sensitive reaction for potassium (CURTICA) 6.

Determining phosphoric acid in acid phosphate. J. F. WILKINSON. U; S.

1,462,840, July 24. Free acid is extd. from a known amt. of acid phosphate with a known amt. of alc. and the soln. is titrated with an alkali metal hydroxide.

## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

**Cassiterite crystals from the New England district, N. S. Wales and Stanthorpe, Queensland.** MARIE BENTIVOGLIO. *J. Proc. Roy. Soc. N. S. Wales* 55, 65-82 (1922).—Twelve selected crystals are described, crystallographically.

**Etched figures of Japanese minerals.** SHIMAMATSU ICHIKAWA. *Am. J. Sci.* 6, 53-72, 137-57 (1923).—The natural etchings of *topaz* crystals, from various Japanese localities, are shown in 9 plates.

**Brugnatellite from Monte Ramazzo (Liguria).** ETTORRE ARTINI. *Atti accad. Lincei* [v], 31, ii, 491-6 (1922).—Analysis of brugnatellite from Monte Ramazzo gives the following results:  $H_2O$  32.42,  $CO_2$  8.00,  $Fe_2O_3$  16.12,  $MnO$  1.77,  $CaO$  1.19,  $MgO$  39.13, insol. residue 0.99, total 99.62. When corrected for the small proportion of extraneous  $CaCO_3$  present, these numbers are in good agreement with those obtained for brugnatellite from Val Malenco (*C. A.* 4, 3182) and with the formula proposed by A., the slight excess of  $Fe_2O_3$  probably existing in the free state as a product of alteration. The results also render evident the distinction between this mineral and pyroaurite, this being borne out by phys. differences (cf. Foshag, *C. A.* 14, 3207). The brucite from which this brugnatellite is derived by epigenesis contains:  $H_2O$  30.37,  $FeO$  1.37,  $MnO$  0.38,  $MgO$  67.96, insol. residue 0.10, total 100.18. If these numbers are corrected for the insol. matter and the  $FeO$  and  $MnO$  are replaced by  $MgO$ , they correspond closely with the compn. of  $Mg(OH)_2$ .

**Issemannite at Ouray, Utah.** F. L. HESS. U. S. Geol. Survey, *Bull.* 750A, 16 pp. (1923).—Beds of shale alternate with beds of sandstone and in the latter Mo minerals are found. These minerals cause the sandstone to be black in color when first mined, but as it weathers it turns various shades of blue. The Mo is in a water-sol. condition as the sandstone when leached gives a blue soln. and when thoroughly leached no Mo is found in the insol. residue. Analysis of Ouray sandstone by Schaller gave 2.37% of  $MoO_3$ . Analysis of the water-sol. salts of Ouray sandstone by Yancey gave 23.85%  $MoO_3$ . The evidence is not conclusive as to the compn. of issemannite though it appears more probable that it is a sulfate than a molybdate.

**Chemical and optical study of the axinite of Prali (Valle della Germanasca).** E. GRILL. *Atti accad. Lincei* [v], 31, ii, 521-4 (1922).—This axinite, d. 3.314, occurring as a pale, violet-red vein in a mass of erratic gneiss, has the compn.:  $SiO_2$  41.26,  $TiO_2$  nil,  $B_2O_3$  4.70,  $Al_2O_3$  18.74,  $Fe_2O_3$  2.02,  $FeO$  6.11,  $MnO$  4.43,  $MgO$  1.75,  $CaO$  19.52,  $H_2O$  ( $-110^\circ$ ) 0.46,  $H_2O$  ( $+110^\circ$ ) 1.25, F trace, total 100.24. These figures correspond with the formula  $H_2O \cdot 8(Ca, Fe, Mn, Mg)O \cdot 3(Al, Fe)_2O_3 \cdot B_2O_3 \cdot 10SiO_2$ , which contains 1 mol. of water less than that established by Whitfield (*Am. J. Sci.* 34, 281-7) and is not reducible to that of an orthosilicate (cf. Ford, *Am. J. Sci.* 15, 195-201 (1903)).

**Argento-jarosite: a new silver mineral.** C. A. SCHEMP. *Am. J. Sci.* 6, 73-5 (1923).—The mineral was found in the 900 ft. level of the Tintic Standard mine, at Dividend, Utah. It is yellow, brilliant, and micaceous in appearance, and is associated with anglesite, barite and quartz. Analysis by the author (confirmed by Schaller, *C. A.* 17, 2548) gave  $Ag_2O$  19.35,  $Fe_2O_3$  41.77,  $SO_3$  27.09,  $SiO_2$  0.60,  $PbO$  1.60, loss on heating to 150 8.20, sum 98.61%; formula  $Ag_2[Fe(OH)_6](SO_4)_2$ . The name argento-jarosite is given on account of the similarity the new mineral bears to plumbo-jarosite.

**Geology and ore deposits of the Creede district, Colorado.** W. H. EMMONS AND E. S. LARSEN. U. S. Geol. Survey, *Bull.* 718, 193 pp. (1923).—The Creede mining district is located in Mineral Co., southwestern Col., and at an elevation of 8700 to 12,050 ft. The mineral production of this district from 1889 to 1920 is valued at over 41 million dollars of which 28.7 million is Ag, and the other metals in order are Pb, Au and Zn. The mining methods and the treatment of ores are described. The principal ore deposits are Ag-Pb fissure veins in rhyolite. Quartz, barite and thuringite are the most abundant minerals, yet 30 other minerals are noted, with short descriptions. The genesis, alteration and enrichment of the ores are explained with special reference to the conditions in the Amethyst Lode. The air in some of the mines con-

tains less than 4% of O, but it has not been detd. whether the gases are of volcanic origin or residual from air that has oxidized ore and gang minerals. L. W. RIGGS

**The Kotsina-Kukulana district, Alaska.** F. H. MOFFIT AND J. B. MERTIE. U. S. Geol. Survey, *Bull.* 745, 146 pp. (1923).—The mineral resources include Au, Ag, and Cu, but the actual production to date consists of a few hundred tons of Cu ore and a small amt. of Au and Ag. The Cu deposits are of 2 types, the stringer lodes and the contact deposits, the latter being less common in this district. Two promising prospects for Au are described. L. W. RIGGS

**Sodium sulfate: its sources and uses.** R. C. WELLS. U. S. Geol. Survey, *Bull.* 717, 40 pp. (1923).—The recent increased foreign demand for  $\text{Na}_2\text{SO}_4$  has greatly stimulated the search for deposits of the natural salt in several of the western states. Mineralogic descriptions are given of mirabilite, thenardite, apthitalite, bloedite, glauberite and hanksite. Equil. diagrams are shown for mixts. of  $\text{Na}_2\text{SO}_4$ , KCl, NaCl, and  $\text{K}_2\text{SO}_4$ , at 0, 25, 50 and 75°, resp.  $\text{Na}_2\text{SO}_4$  is found as a constituent of surface salts or lake waters in many of the dry districts west of the Rocky Mts., and in several foreign countries. These deposits are briefly described. The origin of  $\text{Na}_2\text{SO}_4$  is largely from sulfates in igneous rocks and from sulfides which on exposure are oxidized to sulfates. These dissolve in rain water and the soln. reacts with certain basic compds. forming sol. sulfates. In the long dry season the solns. of sulfates lose their water thus forming a deposit which is added to each year. The uses of  $\text{Na}_2\text{SO}_4$  in the wood pulp and in the glass industries are described. L. W. RIGGS

**The commercial granites of New England.** T. N. DALE. U. S. Geol. Survey, *Bull.* 738, 471 pp. (1923).—This work is a revised and abridged edition of the writer's 4 bulletins and 2 supplementary papers on the com. granites of the states of New England (cf. C. A. 1, 2805; 3, 769; 4, 161; 6, 975). Part I gives a scientific discussion of the origin, nature, modifications, and special features of granite. Part II is an economic discussion embracing the various phys. and chem. tests of granite and their significance, also descriptions of the quarries, varieties of granite, and the production of the 6 states. L. W. RIGGS

**Origin of the deposits of Chilean nitrate.** J. STOKLASA. *Compt. rend.* 176, 1570-3 (1923).—A comparative study of the strata surrounding the Chilean nitrate deposits and the lava bed of Vesuvius and other volcanoes led to the conclusion that the Chilean nitrate is of volcanic origin. Material ejected from volcanoes always contains  $\text{NH}_4$  salts. These are oxidized to nitrates by biochem. means, the rapidity of the oxidation being accelerated by the radioactive character of the materials. The superiority of Chilean nitrate to synthetic nitrate as a fertilizer for sugar beets is attributed to its radioactivity and to its volcanic origin. L. W. RIGGS

**Mineral wealth of northern Africa (Morocco, Algeria, Tunis).** L. JOLEAUD. *Bull. soc. encour. ind. natl.* 132, 124-430 (1920); *Bull. Agr. Intelligence* 12, 26-8.—A description of the deposits of Ca phosphate in the Barbary states, with a discussion of their mode of formation. JOSEPH S. HERBURN

**Recent views on the origin of coal.** W. COTHAN. *Glückauf* 59, 385-90 (1923).—The opinion of Walther (cf. *Allgemeine Paläontologie*, Pt. 1, *Die Fossilien als Einschlüsse der Gesteine*, 107, 157) that the chief material of the coal-forming plants is distinct from the so-called coal flora is refuted. The coal flora has not migrated from sea to land, but, on account of its structure, must have been a true land flora. From a geologic-botanical standpoint, the hypothesis of Donath (cf. C. A. 17, 1776) by which coal plants consisted of cellulose and the lignin hypothesis of Fischer (cf. C. A. 16, 2099) are considered inadequate. From the geologic-botanical point of view, both cellulose and lignin were present in the original substance, but predominately cellulose. C. C. DAVIS

**Lignin as the initial material and the benzene structure of coal.** FRANZ FISCHER AND HANS SCHRADER. *Ges. Abh. Kenntnis der Kohle* 5, 559-66; *Chem. Zentr.* 1922, IV, 1038.—The benzene structure of coal applies to both anthracites and brown coal. C. C. DAVIS

**Old and new ideas about the original coal substance.** FRANZ FISCHER AND HANS SCHRADER. *Ges. Abh. Kenntnis der Kohle* 5, 543-52; *Chem. Zentr.* 1922, IV, 1038.—A summary of ideas concerning the origin of coal which is considered to be lignin alone (cf. preceding abstr.). C. C. DAVIS

**Oil and gas in the Texas panhandle.** W. PRATT. *Nat. Petroleum News* 15 (No. 30), 57-64 (1923).—A general survey of the geological features of this field. D. F. BROWN

**The limestones of the Bolca.** PIO LAMI. *Boll. chim. farm.* 62, 257-61 (1923).—Analyses are reported of 30 distinct strata in a lower Eocene formation in the vicinity

of Mt. Bolca, a region famous for its deposits of fossil fish. Max. and min. values are as follows:

	Loss on ignition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>2</sub>
Max. ....	49.70	29.27	9.64	51.72	1.98	2.65
Min. ....	30.02	4.00	1.63	30.72	0.01	0.06

A. W. DOX

**Clays.** III. Clays of Hammam-Meskoutine. O. BOUDOUARD AND J. LEFRANC *Bull. soc. chim.* 33, 581-7(1923); cf. *C. A.* 17, 1870.—These clays are the same as the kaolins of Djebel-Debar studied by Granger and Bremond (cf. *C. A.* 16, 3453). They are complex, not homogeneous, and do not belong to the kaolin family. They are notably impregnated with sulfates and are more readily attacked by HCl than are the halloysites. IV. **Mechanical analysis.** *Ibid.* 587-97.—The levigation method of Schuitze was employed. From the original compn. of the clays and the compn. of the fractions sepd. by mech. analysis, stoichiometric formulas were calcd. On this basis the clays studied were arranged in 8 groups. This classification accords with that adopted in the porcelain industries.

L. W. RIGGS

\* Occurrence of porphyritic intrusions at Yass, N. S. W. C. W. MANN. *J. Proc. Roy. Soc. N. S. Wales* 55, 180-7(1922).—This preliminary paper gives evidence that these intrusions were formed by quiet deposition, volcanic activity being exceptional.

L. W. RIGGS

**Origin and mode of emplacement of the great tuff deposit of the valley of Ten Thousand Smokes.** C. N. FENNER. Carnegie Inst. Washington, No. 480, *Katmai Series* No. 1, 1-74(1923).—A dynamical study. Chemical study of the fumaroles of the Katmai region. E. T. ALLEN AND E. G. ZIES. *Ibid.* No. 485, *Katmai Series* No. 2, 75-155.—A fumarole is defined as a vent or fissure in the ground from which issue gases of volcanic origin. In practice the term is often applied to the issuing gases. Partial summary: Fumarole temps. in this region in 1919 ranged from 100° to 650°. The borders of the whole fumarolic area were usually of low temp. Fumarolic activity appears to be on the decline. Steam is the predominant constituent in all the gases examd., whatever the temp. In the samples analyzed it varied from 98.65 to 99.85% by vol., allowing for sol. gases. The most important remaining gases are HCl, CO<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub>, HF and sometimes CH<sub>4</sub>. Minor gaseous constituents are O<sub>2</sub>, CO, A, and NH<sub>3</sub>. Ammonia generally occurred in the form of chloride and probably fluoride; it varied greatly in amt. and was not quant. detd. H was detd. with H<sub>2</sub>S. SO<sub>2</sub> may occur but was not detected. The incrustations show that S is sometimes a constituent of the gases, and, more rarely, a sulfide of As. Among sol. gases the percentage of HCl reaches the same order of magnitude as CO<sub>2</sub>, and HF an order of magnitude comparable with that of H<sub>2</sub>S and N<sub>2</sub>. This quantity of F is unique in the annals of volcanology. The relation of A to N is practically the same in the gases as it is in the atm. If the A and N in the gases came from the atm. then the associated O has been chiefly absorbed. The H<sub>2</sub>O of the gases is thought to be largely of surface origin. The heat of fumaroles is not generated by oxidation by atm. O in the surrounding pumice. In none of the fumaroles are combustible gases burning at the surface. No relation between temp. and gas compn. was seen in this region except in the case of sol. gases.

L. W. RIGGS

Synthetic aluminium silicate and its relations to kaolin (SCHWARZ, BRENNER)  
6. A visit to the potassium mines of Alsace (CONY) 18. The genetic relationship between thorium and uranium and the determination of the age of radioactive minerals (KIRSCH) 3.

## 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, R. S. WILLIAMS

**Notes on the present position and recent progress of the various metallurgies.** MARCH, FOURMONT. *Rev. métal.* 20, 262-7, 330-8, 358-68(1923).—A review covering the metallurgies of iron and steel, Cu, Pb, Au and Ag. A. PAPINEAU-COUTURE. **Centrifugal force in metallurgy.** W. MCA. JOHNSON. *Eng. Mining J.-Press* 116, 92-3(1923).—Sepn. of metal or mat from slags might be effected by elec. superheating and rotation induced by a rotary magnetic field. Figures are quoted suggesting that a similar cleaning action occurred in elec. furnace treatment of a complex Zn ore, the slags running as low as 0.01% Pb and 0.05% Cu.

A. BUTTS

**Selective flotation at Simon, Nev.** WM. MACDONALD. *Eng. Mining J.-Press* 116, 48(1923).—Figures are given illustrating the successful treatment of Ag-Pb-Zn ore by this method at the Simon mill.

**Assembling a metallurgical laboratory.** RICHARD RIMBACH. *Blast Furnace Steel Plant* 11, 419-23, 431(1923).

**Trend of metallurgical practice on the Witwatersrand.** A. W. ALLEN. *Eng. Mining J.-Press* 116, 58-61(1923).—Data are tabulated for the 1921 operations of 35 Au properties. Au recovery averaged 63.4%. There has been little change in ore character in the district as a whole, and radical changes, such as all-sliming, are indicated only in a few instances. Finer grinding is being practiced, however, and concn. on corduroy mats has been a success.

**Screen-sorting analyses by hydrostatic separation.** SERGIO BAGNARA. *Eng. Mining J.-Press* 116, 51-4(1923).—The freeing of mineral from gang, which is the only object of crushing prior to concn., cannot be gaged by a screen analysis alone; a combined screen and sorting analysis is required. The sorting analysis of the ore into % mineral and % gang should be based on sp. gr., and can be made best hydrostatically, by setting in a heavy soln. Methylene iodide ( $\text{CH}_2\text{I}_2$ , sp. gr. 3.35) is used; it costs 17 c. per cc., but can be largely recovered after use by fractional distn. The screen analysis is made first and then 10 to 50 g. (weighed) of the sized material is slowly poured on the surface of 25 cc. of  $\text{CH}_2\text{I}_2$ . The mineral at once sinks, while the gang is collected from the surface by brush and spatula, and each product is washed free of  $\text{CH}_2\text{I}_2$  with alc., dried, and weighed. For good sepn. of material 65-mesh, special settling app. is used. A tabulation and plot of a sample screen-sorting analysis are shown. At that mesh where the homothety ratio of the cumulative mineral % to the cumulative ore % becomes constant, the mineral is entirely freed from the gang. The homothetic variation also indicates the amt. of mineral still attached to gang at meshes coarser than this, and may be used in the consideration of middlings. The grade or metal content of middlings at a given mesh also may be predicted by calcn. The method may be applied to expression of the efficiency of concg. devices, detn. of the distribution of Au and Ag between ore components, sp. gr. detns., etc.

**The Trail smelter.** G. H. YOUNG. *Eng. Mining J.-Press* 116, 139-49(1923).—A brief history is given of the development and production of the Consolidated Mining and Smelting Co., in Brit. Columbia, together with descriptions and flow sheets of the Pb and Cu smelting units, the Pb and Cu electrolytic plants, the Zn plant, the Au and Ag refinery and the  $\text{CuSO}_4$  plant.

**Coke quality and blast-furnace operations.** F. W. SPERR, JR., AND D. L. JACOBSEN. *Blast Furnace Steel Plant* 11, 378-83, 426-31(1923).—The injurious effect of the oxidizing zone of the blast furnace lies not only in the increased coke consumption but also in the quality of iron made. Because of the oxidation, large amts. of  $\text{FeO}$  are present in the iron, which cause internal chilling on casting. The oxidizing zone, which controls the  $\text{FeO}$  content, is itself controlled by the combustibility of the coke used. The efficiency of a combustible coke can be shown by charcoal, which burns much faster and at the same time requires but about 65% as much air as coke; there is also required 336 lbs. less charcoal per ton iron and the temp. of the air at the tuyères is  $540^\circ\text{F}$ . lower than with the coke furnace. Deviations from the C-O diagram are explained and the relation of coke combustibility to consumption is discussed. The effect on furnace tops with slowly and rapidly burning cokes affects the gas made and this gas can be used as an indication of the control of the furnace. With fast burning coke and decreased consumption, the  $\text{CO}_2$  to  $\text{CO}$  ratio in the furnace gas rises. For ores difficultly reducible, a certain amt. of reduction of size is recommended, so that a fast burning coke can be used. The physical conditions of the coke and ore should be so gaged as to make the use of fast burning coke possible. The coke varies in combustibility with the temp. of coking. Good coke is produced from coking coals at temps. of from  $1380^\circ$  to  $1520^\circ\text{F}$ . A detn. of the combustibility of cokes is merely qual. at present. In summarizing the nature of coke for the blast furnace various specifications are given.

**Coke and its behavior in the foundry.** H. KOPPERS. *Fuel* 2, 160-5(1923).—The compn. of coked fuel, the process of combustion in blast furnaces and foundry cupolas, the influence of coke on cast-Fe, the combustibility of coke and slow burning foundry cokes are described with diagrams. To the properties considered at present necessary in a blast furnace coke should be added: (1) lumps not to exceed 120 mm. long, (2) a coking temp. of  $660-800^\circ$  (the coke should evolve gas only slowly at this temp.), (3) the volatile constituents not to exceed 3%, (4) when lumps (50-120 mm.) weighing 50 kg. are dropped 4 times from a 1.85 m. height, not over 25% should break into pieces

less than 50 mm. long, (5) 50 kg. of coke (50-120 mm.) revolved in a drum (1 m. diam. and 0.5 m. long) for 4 min. at 25 rev. per min. should give at least 80% lumps over 40 mm. long, and (6) H<sub>2</sub>O should not exceed 3%. All qualities of caking coal should be suitable for blast furnace coke if the product made at a temp. not exceeding 800° is sufficiently strong. For a foundry coke should be added: (1) lumps not over 80-120 mm. long, (2) a coking temp. above 1000° (the coke should evolve gas only above 1000°), (3) a strength and H<sub>2</sub>O content the same as for blast furnace coke. Only good caking coal poor in O (*i. e.*, poor in gas) should be used for foundry coke. According to Osann, dissolved O in foundry-Fe is very harmful and the appearance of hard castings can be accounted for in this way. No successful attempts have yet been made to remedy this. It is proposed to form a layer of slag approx. 400 mm. deep below the fusion zone. The molten Fe, after percolating through this layer, gradually flows into an intermediate chamber from which it is tapped for casting. The slag layer prevents the Fe below the fusion zone from contact with the coke and absorbing more C from the latter. The slag is at a high temp. and if sufficiently basic, the coke has a reducing action and any S absorbed from the coke remains in the slag and slag-free Fe, Mn and Si appear as constituents of the molten metal. New slag flows off and the Fe remaining in the slag can be tapped at the lowest point of the furnace. The arrangement and operation of the cupola become similar to a blast furnace. Fe can be remelted any no. of times without admixt. of expensive ingredients. C. C. DAVIS

**Manufacture of crucible composite steel.** A. W. F. GREEN. *Chem. Met. Eng.* 29, 59-61 (1923).—It is possible to cast crucible steel of different compos. into the same mold, thus producing a variety of composite steels of unique properties. These can be made in no other way. V. O. HOMERBERG

**Reduction of iron oxides by fuel gases.** E. D. EASTMAN. *Bur. Mines, Repts. Investigations* No. 2495, 14 pp. (1923); cf. *C. A.* 16, 1901.—Coal gas, water gas and producer gas of av. compn. were used exptly. at 600° to 1000° to det. the efficiency of reduction of Fe oxides by gaseous reducing agents. *Coal gas*.—If final equil. is obtained coal gas at 600° would reduce FeO but deposit C. About 1/3 of its CH<sub>4</sub> and all unsatd. hydrocarbons would be destroyed. At 700° and above only negligible amts. of CH<sub>4</sub> would remain and C would be no longer deposited. The max. reducing power increases about 12% between 700° and 1000°. CH<sub>4</sub> does not react much up to 800° or higher. The efficiency is thus reduced about 75% and the rate of reduction decreased. Coal gas requires the supply of more heat per kg. of Fe produced than the other gases if its full reducing value is obtained. So long as CH<sub>4</sub> is not used in reduction the heat quantities obtained by combustion of used gas more than compensate for this. *Water gas*.—At 600° water gas oxidizes Fe, deposits C, and would actually form CH<sub>4</sub> in reaching equil. The reverse is true at 700° and above. Between 700° and 1000° a gain of about 10% in max. efficiency is indicated. Inactivity of CH<sub>4</sub> is not very important. The larger proportions of H<sub>2</sub> and CO should be of advantage in obtaining large proportions of the theoretical yields, which are comparable with those for coal gas neglecting CH<sub>4</sub>, or about 1/3 the full yield of coal gas, vol. for vol. From the thermal standpoint, water gas appears to have an adequate margin of safety if good heat interchange is provided. *Producer gas*.—This gas oxidizes Fe and deposits C at 600°. The max. efficiency of reduction at 1000° as compared with 700° is about 30%. Small abs. variations in compn. cause large relative changes in reducing power. Vols. required to effect given reductions are 3 to 15 times larger than those for other gases. The large proportion of N<sub>2</sub> should lower the rate at which reduction is obtained. The thermal margin is not large and heat would probably have to be supplied. J. L. WILEY

**Proposed plan for crushing, grinding, and concentrating low-grade sulfide ore.** ARTHUR CROWFOOT. *Trans. Am. Inst. Mining Met. Eng.* 1256M, 6 pp. (1923).—An outline of the flow-sheet developed for the Morenci Cu mill, Ariz., during 2-yr. operation of a 400-ton pilot mill. A. BUTTS

**Notes on the selection of a copper-smelting plant.** W. A. HEYWOOD. Discussion. *Bull. Inst. Mining Met.* No. 225, 5 pp. (1923); cf. *C. A.* 17, 2100.—A large reverberatory may be compared with a large blast furnace in efficiency and costs, but a small blast furnace has the advantage over a small reverberatory in most cases. A. J. CADDICK: Additions of fuel up to 4% in pyritic smelting caused reductions in slag loss. The greater the vol. of blast fed to the furnace, and the less the fuel used, the greater was the amt. of burden smelted. A. BUTTS

**Chloridizing roasting [of ores.] The system cuprous sulfide-salt.** V. TAPPEL. *Mitt. Kaiser Wilhelm-Inst. Metallforsch.* 1, 58-68 (1922).—By subjecting a mixt. of 1 pt. of Cu<sub>2</sub>S and 4 pts. of salt to a temp. of 250-375° in a slow current of dry air, 1/3 of the total Cu is rendered sol. in water, while the remainder is readily sol. in acids. Only



a relatively small proportion of air is required and no evolution of Cl, SO<sub>2</sub> or SO<sub>3</sub> takes place below 375°.

J. S. C. I.

**Desulfurizing power of iron blast-furnace slags.** R. S. McCaffery and J. F. Oestherle. *Trans. Am. Inst. Mining Met. Eng.* 1254S, 28 pp. (1923).—The solubilities of CaS and MnS were separately detd. in mixts. equiv. to the minerals anorthite (CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>), gehlenite (2CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>), and Ca bisilicate (CaO·SiO<sub>2</sub>). To mixts. of c. p. CaO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> in these proportions were added varying amts. of CaS or MnS; melts were made in graphite crucibles in a resistor furnace, cooling curves were detd., and the resulting slags analyzed. The equil. diagrams of the six systems as thus detd. are shown, and the soly. at different temps. is indicated by the % CaS corresponding to points on the liquidus curve. Al<sub>2</sub>O<sub>3</sub> in slags was found to increase the soly. for CaS and decrease it for MnS. Soly. for both increases rapidly with temp. This is emphasized by diagrams in which soly. and viscosity are each plotted against temp. A rise from 1400° to 1600° multiplies the soly. for CaS by 3 and for MnS by 6; temp. is a greater factor in this respect than chem. compn. of the slag. Other diagrams show S soly. and viscosity plotted against temp. for typical slags of furnaces making basic, foundry, bessemer, and special irons. Soln. of CaS and MnS in the slag is most rapid in the hearth of the blast furnace.

A. Butts

**Improvements in zinc milling in the Tri-state district.** HERBERT H. WALLOWER. *Eng. Mining J.-Press* 115, 1155-7 (1923).—Application of Boylan cones, canvas trays in slime treatment, and belt-conveying systems for tailings disposal have been the principal features. These are illustrated with the flow-sheet of the mill of the Golden Rod M. & S. Co., Tar River, Okla.

A. Butts

**Separation of the cadmium in zinc blendes.** H. J. BORCHGREVINK. *Tidsskrift for Kemi og Bergvaesen* 2, 9-11 (1922).—Zn blende (1000 kg.) from Upper-Silesian works, contg. 0.35% H<sub>2</sub>O, 88% Zn and 2.51% Cd, was digested with 4 cu. m. H<sub>2</sub>O. A stoichiometric amt. of H<sub>2</sub>SO<sub>4</sub> of 60° Bé. was added slowly under agitation. The mixt. was heated for 2 hrs. to 50° and Cd pptd. by an excess of zinc dust (178.4 kg. contg. 3.34% Cd). The spongy Cd ppt. was washed by several decantations with hot water completely to remove the water-sol. Zn, and next gently dried. The output of dried Cd sponge was 95.2 kg. contg. 13.4% H<sub>2</sub>O and 34.12% Cd. This product was distd. in steel muffles by 100 atm. pressure whereby a 99.75% pure Cd was obtained. The total output was 84.39% of the applied Cd, including the amt. contained in the zinc dust used for the pptn. The output was increased by 3% during the following continuous working.

C. H. A. SVERTSEN

**Metallography in America.** H. S. VAN KLOOSTER. *Chem. Age (N. Y.)* 31, 291-2 (1923).

E. H.

**The improvement of cast iron by the addition of nickel.** E. PIWOWARSKY AND K. EBBEFELD. *Stahl u. Eisen* 43, 967-8 (1923).—A high-C cast iron to which Ni was added showed a mechanical betterment of from 25% to 40%. Additions of more than 1% Ni showed no added improvement. With increase of Si in the cast iron the beneficial effect of Ni is lost.

W. A. MUELLER

**Observations on the Schoop metallizing processes and on their recent progress.** J. GUILBERT. *Rev. métal.* 20, 352-7 (1923).—Brief description of the process with a discussion of the mechanism of the adhesion of the film of sprayed metal.

A. P.-C.

**Aluminium from a corrosion point of view.** W. R. DOUGLAS-SHAW. *Beama* 13, 100-4 (1923).—A brief review of the chem. properties of Al and its alloys.

C. G. F.

**Etching figures in microscopical metallography. Contribution to the study of etching reagents.** ALBERT PORTEVIN. *Rev. métal.* 20, 381-97 (1923).—A profusely illustrated review.

A. PAPINEAU-COUTURE

**The thermal treatment of special steels in general and more particularly of chromium steels.** F. MAURER AND R. HOHAGE. *Mittg. X. W. Inst. f. Eisenforschung* 2, 91-105; *Rev. métal.* 20 (Extraits), 288-9 (1923).—A critical review.

A. P.-C.

**Theories concerning the pyrophoric property of cerite metals.** PETER STEINHARDT. *Edel-Erden u. Erzen* 4, 45-7 (1923).—An outline and comparison of the theories of Fettinger (*C. A.* 4, 741, 1863) and of Samter (*C. A.* 4, 3185).

C. C. DAVIS

**Adsorption and adhesion pressure (TRAUBE, NISHIZAWA) 2. Gravity separation of ores (U. S. pat. 1,462,881) 13.**

**Ore flotation apparatus.** J. P. RUTH, JR. U. S. 1,463,405, July 31.

**Electromagnetic mineral separation.** W. M. MORDEY. U. S. 1,463,713, July 31.

**Dissolving values from ores.** A. SILVER. U. S. 1,461,807, July 17. Ores contg.

substances which prematurely ppt. values dissolved from the ore, *e. g.*, Au and Ag ore contg. carbonaceous substances, are treated with substances such as mineral oil which prevent this premature pptn. and are then leached with a suitable solvent, *e. g.*, a cyanide soln.

**Precipitating copper from solutions.** F. LAIST. U. S. 1,461,918, July 17.  $\text{SO}_2$  is introduced into solns. such as those of  $\text{CuSO}_4$  while the soln. is maintained under pressure and at a temp. below that at which substantial reaction occurs and, after introduction of  $\text{SO}_2$  in greater amt. than would sat. the soln. at atm. pressure, the temp. is raised to ppt. Cu substantially free from S compds.

**Obtaining tin from ores.** H. H. ALEXANDER. U. S. 1,461,957, July 17. Sn ore, *e. g.*, Bolivian Sn ore contg. Fe, Sb, Pb and Bi, is treated in a blast furnace with a small amt. of C or other admixture which will cause the formation of Sn silicates and the latter are removed as a slag and reduced with CaO and additional C.

**Metallurgical furnaces.** M. PASCHKE and E. SCHIEGRIES. Brit. 191,648, Mar. 4, 1922. Fittings such as blast tuyères and their protective casing, cooling plates and beams and hot-blast valves for metallurgical furnaces are made of Al or its alloys, a suitable alloy contg. 8% of Cu and 92% of Al. The surface of the fittings may be oxidized, *e. g.*, by dipping in dil.  $\text{HNO}_3$  or by directing a blast of highly heated air on them, or it may be covered by a plastic material, the chief component of which is clay.

**Metals and alloys.** W. L. TURNER. Brit. 191,167, Oct. 8, 1921. In the production of metals and alloys such as Mn, Co, Fe-W, Fe-V and Fe-Ti by a thermo aluminic process, a portion of the reaction mixt. contains Al in powdered or finely granulated form, and another portion contains Al in relatively large pieces, the two portions being brought into reaction successively or together. In some cases, as in the manuf. of Fe, practically all the Al may be in the larger form. Cf. 123,103 (C. A. 13, 1444).

**Wrought iron.** A. SAUVEUR. U. S. 1,463,228, July 31. The C content of molten pig Fe is reduced by Bessemer action, retaining slag and Fe oxide produced by this action in the decarbonized Fe. The temp. of the product is then lowered while subjecting it to continued cascade agitation and a wrought Fe "ball" is thus obtained.

**Balling scrap metal.** J. M. SELLERS. U. S. 1,463,539, July 31. Wrought Fe is prepd. from scrap metal by preheating the latter without melting it and then balling the preheated scrap by rolling it in a rotary furnace while subjected to direct action of fresh combustion gases.

**Casting magnesium and its alloys.** A. BECK, K. GERSBACH and O. H. WEBER. U. S. 1,463,609, July 31. Molds for casting Mg, Mg alloys or similar readily oxidizable metals are dusted with a substance such as S or Mg oxalate which on contact with the molten metal will give off a gas more readily oxidizable than the metal to be cast.

**Ingot mold.** A. A. CLAASSEN. U. S. 1,463,771, July 31. Bars are arranged within the upper part of the mold to compress its contents.

**Furnace for carbonizing steel or iron.** N. OLSEN. U. S. 1,463,438, July 31.

**Steel-heating furnace.** J. HUNDLEY. U. S. 1,462,639, July 24. The furnace is provided with conveyors for handling materials and for removing slag or cinder and with brushes for freeing the conveyor from the conveyor surfaces.

**Heat treatment of light castings.** S. APGAR. U. S. 1,462,460, July 17. Mn-steel chain or other light castings are heated in an environment which will protect them from decarburization and from oxidation.

**Coating for metals.** W. H. MILES and R. J. WHEATLEY. Brit. 191,529, Nov. 7, 1921. A compn. for coating metal surfaces consists of portland or other hydraulic cement, a binding agent, which may be casein, blood serum, egg albumin, algin, vegetable protein, or gelatin, and a little resin, with or without coloring matter,  $\text{H}_2\text{O}$  being used as a vehicle. The compn. may be hardened after application by means of  $\text{HClO}_4$ .

**Fluxes.** P. GREEN. Brit. 191,436, Oct. 6, 1921. For welding cast Fe by the oxy-acetylene process a flux consists of 20 parts by wt. of calcined  $\text{Na}_2\text{CO}_3$ , 4 parts of  $\text{NaHCO}_3$ , 4 parts of borax, and 1-6 parts of ferro-silicon, the proportion of which is varied according to the degree of softness required for the weld.

## 10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER and CLARENCE J. WEST

**Diamond and graphite structure in organic compounds.** A. SCHLEICHER. *J. prakt. Chem.* 105, 350-4(1923).—A theoretical discussion of the structure of aliphatic-aromatic compds. and the possibility of the rearrangement of the two types of structures into one another. C. J. West

**Freezing points of organic substances. VII. JEAN TIMMERMANS.** *Bull. soc. chim. Belg.* 31, 389-97(1922); cf. C. A. 16, 2304.—The f. ps. of a further 68 org. liquids are given in tabular form. The results confirm T.'s previous conclusion that the alternation of m. ps. between the odd and even members of a homologous series is a general phenomenon, and allow this generalization to be extended to include substances possessing two hydrocarbon chains linked by a central characteristic group (secondary amines, ethers, alkyl sulfides, etc.). Inverse alternation, in which the odd members of a series melt at a higher temp. than the adjacent even members, is shown to be frequent, even in series of sym. compds. The m. ps. of the higher terms of all the homologous series considered tend towards a common value of  $117^\circ$  and, further, for the paraffins and most of their monosubstitution derivs., it is found that the  $C_{10}$  member m.  $65^\circ$ , the  $C_{12}$  member about  $20^\circ$ , and the  $C_8$  member about  $-45^\circ$ . Compds. contg. an  $NH_2$  or a  $HO$  group do not conform to this rule, their m. ps. being always higher than those quoted above. Among the lower members of a series there is often considerable and irregular variation in the m. ps. of successive members, but a minimum is usually observed at about the  $C_4$  term. J. C. S.

**Lignite primary tar.** E. FROMM AND H. ECKARD. *Ber.* 56B, 948-53(1923).—Two primary tars from Miocene lignites from the mines "Louise" (I) and "Grefrath" (II), resp., near Cologne were sepd. into their neutral, acid-sol. (about 0.005%) and alkali-sol. (about 20%) components. The neutral part, volatile with steam, of I b.  $140-240^\circ$  and the d. of the individual fractions increases uniformly from 0.835 to 0.895; that of II b.  $115-240^\circ$  (18% b. below  $140^\circ$ ) and d. covers the range 0.819-0.897 (for the fraction b.  $115-60^\circ$ , the d. is 0.823-0.832, indicating the accumulation of a definite compd.). These fractions contain a small amt. of O removed only with difficulty by repeated distn. from Na, whereby is obtained a terpene-like substance,  $C_{10}H_{14}$ , or  $C_{11}H_{16}$ , b.  $185^\circ$ , d. 0.8569, mol. wt. in  $C_{10}H_{14}$  150.2-7.7. From the neutral part of I non-volatile with steam were isolated the paraffins  $C_{25}H_{52}$ , m.  $46^\circ$ ,  $C_{26}H_{54}$ , m.  $52^\circ$ ,  $C_{27}H_{56}$ , m.  $57.5^\circ$ ,  $C_{28}H_{58}$ , m.  $62^\circ$ ,  $C_{29}H_{60}$ , m.  $69.6^\circ$  and  $C_{30}H_{62}$ , m.  $73^\circ$ . The acid-sol. part of I yielded  $C_8H_{16}$ , that of II a base yielding a hydrated oxalate, m.  $177-8^\circ$  after drying *in vacuo* at  $118^\circ$  and having a compn. corresponding to a picoline oxalate,  $2C_8H_7N_3 \cdot 3(CO_2H)_2$ . The alkali-sol. parts, volatile with steam, yielded a cresol, several phenols  $C_8H_7OH$  and a phenol  $C_8H_7OH$ , isolated as the phenylurethans, only 1 of which (that of *m*-cresol) was identical with a previously known compd. The following *phenylurethans* were prepd. from the pure phenols for purposes of comparison: *p*-cresyl, m.  $115^\circ$ ; *p*-xylenyl, m.  $162^\circ$ ; *sym*-xylenyl, m.  $151^\circ$ ; *asym*-xylenyl, m.  $102^\circ$ . C. A. R.

**Thermal decomposition of tetramethylammonium fluoride.** F. GONZÁLES NÚÑEZ. *Anales soc. españ. fis. quim.* 20, 539-49(1922).— $Me_4NHF$  was obtained in 89% yield by exact neutralization of the hydroxide with  $HF$ . It was impossible fully to dry the compd. as it is fully as hygroscopic as  $P_2O_5$ . When decompd. by heating in presence of water with metallic catalysts (Cu, Ag, Pt) the products are  $N_2O$ ,  $MeF$ ,  $NMe$ , and  $CH_4$ . Cu is the most active catalyst. The very elaborate app. used is illustrated.  $CH_4$  dissolves in liquid  $MeF$ , forming a mixt. of constant b. p.,  $3.5^\circ$ . This mixt. could not be sepd. by diffusion. The wt. of a normal l. is 1.5563 g., corresponding to 1.2%  $CH_4$ . L. E. GILSON

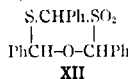
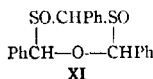
**Bismuthobromoacetates, mixed organometallic complexes.** A. C. VOURNAZOS. *Bull. soc. chim.* 33, 699-702(1923).—The complexes formed by salts of org. acids with Sb and Bi halides are more stable than those formed with the free acids. To a boiled 10% soln. of  $NH_4OAc$  in  $AcOH$  a hot 10% soln. of  $BiBr_3$  was added. The  $NH_4$  bismuthobromoacetate crystg. on cooling was washed with  $AcOH$  and dried in a desiccator. It is difficultly sol. in  $AmOH$  and  $AcOH$ , and is decompd. by cold  $H_2O$ , giving  $BiOBr$ . Analogous K, Na, and Li bismuthobromoacetates were prepd. A 10% soln. of  $BiBr_3$  in  $AcOH$  was added to  $MeNH_2$  in warm  $AcOH$ , giving *MeNH*<sub>2</sub> bismuthobromoacetate, yellow prisms, decompd. by  $H_2O$ . Similar  $EtNH_2$ ,  $PhNH_2$ , and *o*- $MeC_6H_4NH_2$  bismuthobromoacetates were prepd. A. C. PURDY

**Some complex organic compounds of bismuth.** E. MOLES AND R. PORTILLO. *Anales soc. españ. fis. quim.* 20, 571-6(1922).—Preliminary data are given on the prepn. and properties of bismuthotartaric acid, bismutholactic acid, and bismuthochitic acid. J. C. S.

**Isomerism of the thioaldehydes.** EMIL FROMM AND CARLTHERO SCHULTIS. *Ber.* 56B, 937-47(1923).—The theory of Fromm that the trithioaldehydes are cyclic sulfides capable of existing in *cis*- and *trans*-forms (I and II) demands that there be but one form each of trithioformaldehyde (III) and trithioacetone (IV). The discovery by Hinsberg of what he supposed to be a 2nd  $\beta$ -III and a 3rd ( $\delta$ -form) of trithiobenzaldehyde (V) led him to propose a theory of S isomerism involving 2 valence centers in the S atom.

The crude product (VI) obtained from HCHO and H<sub>2</sub>S in the presence of HCl has the same m. p. (216°) as pure III but is not III, for with concd. HI it gives a product (VII), decmps. 247°, which has approx. the compn. (CH<sub>2</sub>S)<sub>2</sub> and changes into pure III in all attempts to recryst. it, while III never gives VII with HI. On oxidation both VI and III give sulfoxides of approx. the same compn. but while that from VI yields VII with HI, the sulfoxide (VIII), m. 270°, from III regenerates pure III. Baumann has shown that the primary products of the action of H<sub>2</sub>S on HCHO are complex bivalent mercaptans (HSCH<sub>2</sub>SH, HSCH<sub>2</sub>SCH<sub>2</sub>SH, etc.) which are easily oxidized by the air to the corresponding disulfides. VI is probably such a disulfide of the general formula S.CH<sub>2</sub>.S.CH<sub>2</sub>.....S.CH<sub>2</sub>.S, or (H<sub>2</sub>CS)<sub>x</sub> + S; the difference in compn. between this and

(H<sub>2</sub>CS)<sub>x</sub> falls within the limits of exptl. error when x is 12 or more. VII would then be the dimercaptan, (H<sub>2</sub>CS)<sub>2</sub> + H<sub>2</sub>S, corresponding to VI. II's δ-V, m. 180-90°, is merely impure β-V; his chief error is his belief that α- and β-V yield different products with H<sub>2</sub>O<sub>2</sub>. As a matter of fact, both give with the corresponding aunts, of H<sub>2</sub>O, a *trisulfoxide* (IX), a *trisulfone* (X) and a *tribenzal oxide disulfoxide* (XI) or *oxide thiosulfone* (XII); all other oxidation products, like H's tetroxide and pentoxide, are mixts. contg. the above 3 compds. The latter are stable towards aq. alkalis and can be sepl. from each other by treatment with alkali; in this treatment BzH and SO<sub>2</sub> are always formed, indicating that the mixts. also contain alkali-unstable components. Reduction of IX gives a substance, generally contg. I and m. 180-215°, which on recrystn. yields pure β-V, m. 226°. With a large excess of hot H<sub>2</sub>O<sub>2</sub>, α- and β-V give a mixt. which with aq. alkali yields X, XI, BzH and SO<sub>2</sub>. There is no reason, therefore, for abandoning F.'s theory to explain the isomerism of the trithioaldehydes. Pure III and 1 mol. I<sub>2</sub> boiled a short time in CHCl<sub>3</sub> give a dark red *diiodide*, C<sub>6</sub>H<sub>5</sub>SiI<sub>2</sub>, m. 100-10°, dissociated into III and I by hot alc., Et<sub>2</sub>O and Me<sub>2</sub>CO and by cold dil. acids and alkalis; with 2 or more mols. I is obtained a dark violet *tetraiodide*, decmps. 100-5°, dissociated in the same solvents as the diiodide, also in freezing C<sub>6</sub>H<sub>6</sub> (mol. wt. found, 253.1). IX, from α- or β-V and 3 equivs. H<sub>2</sub>O<sub>2</sub> in AcOH in the cold or at 90-100°, m. 240°, is perfectly stable towards boiling aq. NaOH but is at once dissolved and completely decmpl. by cold alc. NaOH. With a large excess of H<sub>2</sub>O<sub>2</sub> is obtained a mixt., decmps. 295°, sepl. by NaOH into a fraction which decmps. into BzH and Na<sub>2</sub>SO<sub>3</sub>, X (which dissolves as the Na salt), and XI (or XII), insol. in NaOH, m. 195°, stable towards concd. H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> and reducing and oxidizing agents. X, pptd. by mineral acids as a chalky



powder, does not m. 340°; *pyridine salt*, C<sub>21</sub>H<sub>13</sub>O<sub>5</sub>S<sub>3</sub>C<sub>6</sub>H<sub>5</sub>N; Na and K salts, decomp. about 300°; *di-Me deriv.*, from X, MeI and alkali in boiling alc., m. 248°, dissolves in hot alkali. C. A. R.

**Catalytic reduction of aliphatic azines. II. Reduction of dimethylketazine and of isobutyraldazine in the presence of acetic acid.** K. A. TAIPALE. *Ber.* 56B, 954-62 (1923).—The reduction of (Me<sub>2</sub>C:N)<sub>2</sub> to (Me<sub>2</sub>CHNH)<sub>2</sub> in the presence of Pt black, described in the 1st paper, has been found applicable to other aliphatic ketazines and aldazines, but the reaction is slow (10-20 g. ketazine requires 75-100 hrs. for its reduction) and the yield of hydrazine is only 60%, the rest of the azine being converted into the corresponding primary and sec. amines. By the proper use of solvents, however, these disadvantages of the method can be overcome. Thus, 11.2 g. (Me<sub>2</sub>C:N)<sub>2</sub> dild. with 25 cc. AcOH absorbs the calcd. amt. of H in 20 hrs. and gives 90% (MeCHNH)<sub>2</sub> (larger amts. of AcOH diminish the yield), together with the primary and sec. amines and also some NH<sub>3</sub>. With (Me<sub>2</sub>CHCH:N)<sub>2</sub>, which is more easily decmpl. by AcOH, the yield of hydrazine is smaller (60%) and that of the amines and NH<sub>3</sub> larger, but with about 1 equiv. AcOH in alc. or Et<sub>2</sub>O, about 80% hydrazine can be obtained (under the same conditions (Me<sub>2</sub>C:N)<sub>2</sub> gives 95% hydrazine). By this method were also prepd. *hydrazo-α-methylpropane-HCl*, m. 146-7°, and *hydrazo-α-ethylpropane-HCl*, m. 172-3°. The following derivs. of *sym-diisopropylhydrazine* (I) are described: di-HCl salt, converted by drying at 55° or crystg. from abs. alc. into the mono-HCl salt, sinters 200°, m. 203-4°; *perchlorate*, m. 145-6°; Me<sub>2</sub>CHNNH(CHMe<sub>2</sub>)CONH<sub>2</sub>, m. 103-4°, from the HCl salt and KCNO; Bz deriv. of I, m. 44.5°; Me<sub>2</sub>CHNNH:CMe<sub>2</sub>, b. 88-8.5°, from I and NH<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>. (Me<sub>2</sub>CHCH<sub>2</sub>NH)<sub>2</sub>, b. 84-4.5°; di-HCl salt, can be recrystd. from EtOH-Et<sub>2</sub>O; mono-HCl salt, m. 175°; *perchlorate*,

m. 159° (decompn.); *di-Bz deriv.*, m. 79-80°; *1,2-diisobutylsemicarbazide*, m. 132°. The mixts. of amines resulting as by-products of the above reductions were isolated as the  $\text{PhSO}_2$  derivs.  $\text{PhSO}_2\text{NHCH}_2\text{CHMe}_2$ , m. 52.5-3.0°, dissolves easily in alkalis;  $\text{PhSO}_2\text{N}(\text{CH}_2\text{CHMe}_2)_2$ , m. 56.5-7.0°, is insol. in alkalis.  $\text{Me}_2\text{CHCH}_2\text{NH}_2\cdot\text{HCl}$ , hygroscopic scales, m. 177-8°;  $(\text{Me}_2\text{CHCH}_2)_2\text{NH}\cdot\text{HCl}$ , m. 260-5° in a sealed capillary, forms a yellow *chloraurate*, decomp. 199-200°. ADDENDUM. *Ibid* 1247.—Owing to the lack of most of the foreign literature in Russia in recent years, T., when he published the above article, was unaware of the papers of Lochte, Noyes and Bailey (*C. A.* 16, 904; 17, 267), the appearance of which has since been called to his attention but which he had not yet seen himself. C. A. R.

**Studies in esterification. I. Esterification of the cycloparaffin monocarboxylic acids.** G. D. ADVANI AND J. J. SUDBOROUGH. *J. Indian Inst. Sci.* 6, pt. 3, 41-68 (1923).—In extending the earlier work on the relation between constitution and rate of esterification of acids a study has been made of the effect of the closing of the ring and the formation of a cyclic structure upon the rate of esterification of an acid. For this purpose the following acids were studied:  $\text{Me}_2\text{CHCO}_2\text{H}$  (I),  $(\text{CH}_2)_2\text{CHCO}_2\text{H}$  (II),  $\text{MeEtCHCO}_2\text{H}$  (III),  $(\text{CH}_2)_3\text{CHCO}_2\text{H}$  (IV),  $\text{Et}_2\text{CHCO}_2\text{H}$  (V),  $(\text{CH}_2)_4\text{CHCO}_2\text{H}$  (VI),  $\text{EtPrCHCO}_2\text{H}$  (VII) and  $(\text{CH}_2)_5\text{CHCO}_2\text{H}$  (VIII). Methods of prep. for the cyclo acids are given in some detail. Expts. on the esterification of  $\text{EtCO}_2\text{H}$  were first carried out which showed that the values obtained could be directly compared with those given by Goldschmidt and Uddy (*C. A.* 2, 261). The values obtained with acids I to VIII confirm their conclusion that when their equation  $K = (1/c) \{ (n+r+a) \log [a/(a-x)] - x \}$  is used, the results vary somewhat with the concn. of the HCl used as catalyst. With 0.02 *N* HCl the values for *K* tend to diminish as the time increases; with 0.1 *N* catalyst the values are fairly const. or slightly irregular, but with more concd. HCl (above 0.2 *N*), the tendency is for the values of *K* to increase with time. The reported results confirm another conclusion of G. and U., that the const. is not absolutely proportional to the concn. of the catalyst. With lower concn. of catalyst (0.02 *N*) the consts. are relatively higher than with 0.1 *N* soln. In the case of an acid which esterifies rapidly the consts. obtained with a 0.02 *N* catalyst do not tend to fall to the same extent as in the slower reactions. It is probable that the increase or decrease of the values of *K* with the time is rather a question of time than of concn. of the catalyst. In the case of the disubstituted acetic acids examd., I is esterified most readily and V and VII least readily. Apparently the Me group has the smallest inhibiting effect and the Et and Pr groups have practically the same effect. The consts. for the 2 groups of acids are: I, 0.156, II, 0.032; III, 0.038, IV, 0.544; V, 0.0031, VI, 0.196; VII, 0.0031, VIII, 0.081. These give the ratios of cyclo acid to corresponding satd. acid: tri-ring, 0.25:1; tetra-ring, 0.13:1; penta-ring, 0.80:1; hexa-ring, 0.28:1. These results are in harmony with Menshutkin's on the acetylation of alc. insofar as the greatest increase in the consts. is noticed on the  $(\text{CH}_2)_5$  series and decreases in the  $(\text{CH}_2)_6$  series. If the cyclo acids alone are considered, the ratios are: II, 1; IV, 16; VI, 7; VIII, 8. In 1 expt. an alc. was used with 0.55%  $\text{H}_2\text{O}$  or 0.24 mols. per l. As the reaction proceeds the value of *k* does not decrease so rapidly as when abs. alc. is employed. C. J. WEST.

**Oxidation of reduced glutathione and other sulphydryl compounds.** MALCOLM DIXON AND H. E. TUNNICLIFFE. *Proc. Roy. Soc. London* 94B, 266-97 (1923).—The reduction of methylene blue by sulphydryl compds. (reduced glutathione, cysteine, and thioglycolic acid) is an autocatalytic reaction. The active agent in the production of this catalysis is the disulfide R.S.S.R. Evidence exists that a more active addn. compd. of RSH with R'.S.S.R' is formed. Disulfide compds. also catalyze the oxidation of sulphydryl compds. by atm.  $\text{O}_2$ . In the autooxidation of glutathione and cysteine (but not of thioglycolic acid) the optimum reaction velocity occurs at  $p_{\text{H}}$  7.4.

JOSEPH S. HEPBURN

**Xanthyl derivatives of allophanic acid, thiosinamine and allantoin.** R. FOSSÉ AND A. HIEULLE. *Compt. rend.* 176, 1719-21 (1923).—Et allophanate in 50%  $\text{HOAc}$  yields with xanthidrol in  $\text{HOAc}$ , Et xanthylallophanate,  $\text{EtO}_2\text{CNHC(NHCH}_2\text{C}_6\text{H}_4\text{O}_2\text{C}_6\text{H}_4)_2$ , m. 230°. By similar condensation xanthylthiosinamine,  $\text{C}_6\text{H}_5\text{NHC(NHCH}_2\text{C}_6\text{H}_4\text{O}_2\text{C}_6\text{H}_4)_2$ , m. 165° (decompn.), and xanthylallantoin (I), m. 215°, were prepd. I may be used to identify allantoin in biochem. solns. I. P. ROLP.

**Reactions of the amino acids. Notes on the *dl*-leucines.** JOHN MISSENDEN AND F. E. LISCHEIT. *Chem. Trade J.* 72, 757 (1923).—Three methods are suggested for the prep. of *dl*-leucine. It may be sep'd. by conversion into a metallic salt which is pptd. by MeOH. The *l*-ester is hydrolyzed when pancreatin reacts upon the Et ester

*Acta* 6, 617-21 (1923).—P. and P. showed that glucosan (I) polymerizes to a diglucosan (II) ( $C_{12}H_{20}O_8$ )<sub>2</sub> and since I is 1,2-anhydroglucose (CRAMER AND COX, C. A. 17, 987) the constitution of II can only be expressed by

The sources of the rare sugars. II. History of raffinose, its discovery and methods of preparation. T. S. HARDING. *Sugar* 25, 82-3 (1923); cf. C. A. 17, 1164, 2103. An extensive bibliography is presented. The method of Clark (C. A. 13, 2011) is reported as being unsatisfactory. Extn. of black oak bark with 5 parts of boiling water and concn. *in vacuo* after filtering gives a sirup from which quercitrin crystals easily. This is hydrolyzed with 0.4%  $H_2SO_4$ , filtered, leaded and treated with  $H_2S$  to remove the excess Pb. After evapn. *in vacuo* to 75% solids the mass crystals, at once, giving a yield of 0.75-1.0% of the bark used. The method of Walton (C. A. 15, 680) is recommended as giving the best yield of raffinose. V. History of melizitose, its discovery and methods of preparation. *Ibid* 240-1.—The occurrence of melizitose in mannas is given as the early source of this sugar. It occurs in comparatively pure condition. The com. prepn. of melizitose includes the alc. extn. of honey produced in dry seasons in regions where conifers abound. The comb and sugar are heated in water to melt the sugar. The wax is removed and may be re-extd. After clarification and filtration the soln. is evapd. Fermentation may be used to remove the reducing sugars. Yields of 5-22% are reported. VI. History of raffinose, its discovery and methods of preparation. *Ibid* 808-10.—An extensive discussion is given. Criticism is made of the methods of Zitkowski (C. A. 4, 3310; 5, 1203), Kodyl (C. A. 8, 1682), Hudson and Harding (C. A. 8, 3777) and Clark (C. A. 16, 1566). The following method is applicable to com. work and eliminates the formation of an intermediate compd. in the process of purification: Six kg. cottonseed meal are extd with 30 l. tap water contg. 750

g.  $\text{Al}_2(\text{SO}_4)_3$ . After a brief stirring the liquid is sepd. in a centrifuge. Paraffin oil is added to prevent foaming, the liquid is concd. *in vacuo* to 3 l. Six l. of 80% alc. are added, stirred well and allowed to stand overnight. The supernatant liquid is siphoned off and the  $\text{Al}_2(\text{SO}_4)_3$  cake washed twice with 80% alc. The alc. ext. is pptd. with basic Pb acetate, filtered and the ppt. washed. Excess Pb is removed with  $\text{H}_2\text{S}$ . Filtration is followed with a norit decolorization. The alc. is distd. off and recovered. Another norit treatment at 95° in the presence of a trace of  $\text{H}_3\text{PO}_4$  gives a clear soln., which is concd. *in vacuo* to 300 cc.; 95% alc. contg. 1%  $\text{HNO}_3$  is added to satn. at 2–10°; seeds are added and the mass is placed in cold storage. The cake formed is crushed and macerated with 80% alc. contg.  $\text{HNO}_3$ , filtered and washed free from color with 80% alc. contg.  $\text{HNO}_3$  and then with 95% alc. For recrystn., soln. is effected in 85% alc. contg.  $\text{HNO}_3$ , impurities are removed by filtration with norit, the alc. is removed by distn. and 95% alc. added to the sirup. Crystn. proceeds rapidly and alc. is added to prevent solidification. A yield of 2.25% is the av. VII. History of maltose, its discovery and methods of preparation. *Ibid* 350-2.—Extensive references are made to the early work on maltose. For the best results in saccharification barley flour is preferred. 2.5 kg. of sol. starch are dissolved in 20 l. hot water. On cooling to 60° 100 g. barley flour are added and allowed to stand overnight. The liquid is concd. to 3 l. and 5.5 l. alc. added, with vigorous stirring for 30 min. After settling the alc. soln. is decanted, and the dextrin washed 15 min. with 2.75 l. alc. A third washing is suggested. The alc. exts. are concd. *in vacuo* to less than a l. vol. Clarification with norit may be made at this point. 95% alc. contg. 1%  $\text{HNO}_3$  by vol. is added to the point of satn. at 10° or lower. After seeding crystn. proceeds rapidly. The crystal mass is macerated with alc. and spun in a centrifugal. One crystn. gives a very pure product in 20% yield. C. H. CHRISTMAN

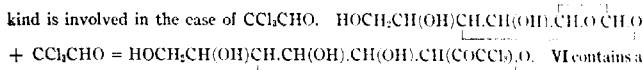
**Oxidation of cane sugar by nitric acid.** F. D. CHATTAWAY. *Science Progress* 17, 598-9(1923).—An historical resumé of this reaction from the time of Bergman (1776) to the present. Oxalic and mesoxalic acids are the chief products. J. S. HEPBURN

**Carbohydrates. III. The action of phosphorus pentachloride upon octaacetyl-maltose.** P. BRIGL AND P. MISTELE. *Z. physiol. Chem.* 126, 120-9(1923); cf. C. A. 17, 1432.—*r*-Chloro-2(?)-trichloroacetylhexaacetylmaltose, prepd. from maltose acetate and  $\text{PCl}_5$  at 104–5° and repeatedly recrystd. from  $\text{Et}_2\text{O}$ , m. 132–3°,  $[\alpha]_D^{15}$  58.65°. Sapon. with  $\text{NH}_3$  in  $\text{MeOH}$  yielded maltose. R. L. STEHLE

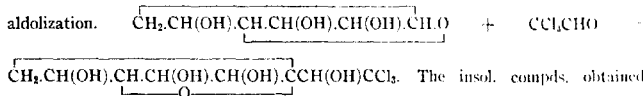
**A new sugar, procellose, obtained by starting with cellulose.** GABRIEL BERTRAND AND MILLE S. BRNOIST. *Compt. rend.* 176, 1583-7(1923).—The octaacetate is prepd. from filter paper by the action of  $\text{Ac}_2\text{O}$  (b. 135–40°), and  $\text{H}_2\text{SO}_4$  (d. 1.835). The alc. mother liquor from the crystn. of the octaacetate contains the new sugar as an acetate. It is liberated from the acetate by adding  $\text{KOH}$ , then  $\text{HClO}_4$  to remove the K. After several purifications in alc. there is obtained 1–2 parts of the new sugar per 100 of original cellulose. The sugar deposits slowly from 85% alc. as sphero-cryst. crusts contg. 2 mol.  $\text{H}_2\text{O}$ . *In vacuo* over  $\text{H}_2\text{SO}_4$  it quickly loses 1 mol.  $\text{H}_2\text{O}$ , but to remove the second mol.  $\text{P}_2\text{O}_5$  or heat to 90° must be used. In the air cellose rapidly takes up its  $\text{H}_2\text{O}$ . It appears to be a trisaccharide of glucose,  $\text{C}_{18}\text{H}_{32}\text{O}_{16}$ . It is very sol. in  $\text{H}_2\text{O}$ , insol. in cold alc., m. 210°. An aq. soln., 1 to 20, after standing 24 hrs. gives  $[\alpha]_D$  22.8° at 21°. It forms an osazone contg. 8.12% of N. Its reducing power is 0.5 that of glucose. By heating with dil.  $\text{HCl}$  its reducing power increases. Two structural formulas are proposed, one as an open, the other as a closed chain. L. W. RIGGS

**Action of chloral on glucosans.** AMÉ PICTET AND F. H. REICHEL. *Helvetica Chim. Acta* 6, 621-7(1923).—A brief historical outline of the action of  $\text{CCl}_3\text{CHO}$  on glucoses (I) is given. The reagents interacted in the presence of  $\text{HCl}$ . P. and R. thought it advisable to study the action using  $\text{H}_2\text{SO}_4$ . Glucosan (II) and  $\text{CCl}_3\text{CHO}$  were stirred in a mortar with  $\text{H}_2\text{SO}_4$  until the odor of  $\text{CCl}_3\text{CHO}$  disappeared and poured into  $\text{H}_2\text{O}$ . A small amt. of resinous material sepd. which slowly transformed into a powder. The filtered acid soln., neutralized with  $\text{CaCO}_3$  and concd., deposited crystals of parachloralose (Hanriot and Richet, *Compt. rend.* 116, 63(1893)). There was no trace of chloralose. Levoglucosan (VI) when treated similarly gave isodichloralglucoses, products insol. in  $\text{H}_2\text{O}$  which were sepd. by filtration. Chloralose, m. 187°, was formed (Meunier, *Bull. soc. chim.* [3] 11, 125(1894)). No parachloralose (VII) was present. Chloraloses (III) hitherto have been made by treating  $\text{CaH}_2\text{O}_4$  with  $\text{CCl}_3\text{CHO}$  and it has been considered that an addn. product first forms and decomps. with loss of  $\text{H}_2\text{O}$ . The view cannot be adhered to when it is known that III result directly when  $\text{CCl}_3\text{CHO}$  is treated with the anhydrides of I, II and VI.  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  remove the  $\text{H}_2\text{O}$ . It has been known for some time (*Compt. rend.* 103, 1461(1886)) that I in  $\text{HCl}$  and also in  $\text{H}_2\text{SO}_4$  is dehydrated and then polymerization is effected

and these reactions progress in the presence of  $\text{CCl}_3\text{CHO}$ , the addn. taking place prior to the polymerization. P. and R. consider the **III** as simple addn. products of  $\text{CCl}_3\text{CHO}$  and the 2 glucosans. The great stability of **III** towards acids shows that the components are joined at a C atom and not at an O atom, and the products contain 4 alc. OH groups (tetrabenzoate of Hanriot). The two **III** subjected to oxidation give  $\text{CO}_2$  and monobasic C<sub>2</sub> acids, and contain the  $\text{CCl}_3\text{CHO}$  group. **III** do not reduce Fehling soln. and the C in the 1-position has, therefore, participated in the condensation. Chloralose is obtained from **VI** and is a  $\beta$ -deriv. of **I**; **VII**, being prepd. from **II**, is an  $\alpha$ -deriv. The chem. properties of these derivs. are very dissimilar, and the transformation of one into the other has not been observed. It is logical to admit that they differ not only in their configuration but in their constitution. **II** readily gives addn. products by reason of the easy breaking of the ethylene oxide ring and probably a reaction of this



hexamethylene oxide ring which is much more stable and with  $\text{CCl}_3\text{CHO}$  this compd. probably combines in accordance with the views of the earlier observers, by



The insol. compds. obtained when the reaction mixt. of  $\text{CCl}_3\text{CHO}$  and **II** is turned into  $\text{H}_2\text{O}$  are designated *trichloralglucoses A and B* and may be sepd. by soln. in boiling alc. A is a cryst. compd., m.  $268^\circ$ ; 0.041 g. dissolves in 100 g. abs. alc. at  $25^\circ$ , 0.053 g. in 100 g. glacial HOAc, 0.120 g. in 100 g. in  $\text{Et}_2\text{O}$ . The mono-Ac deriv., m.  $198^\circ$ , was obtained by the use of  $\text{Ac}_2\text{O}$ . The B compd. m.  $85^\circ$ . A and B do not reduce Fehling soln. after long boiling and are not oxidized by  $\text{KMnO}_4$  or fuming  $\text{HNO}_3$ . H. E. W.

**Lignin and its relation to coal.** AMÉ PICTET and MADELEINE GAULIS. *Helvetica Chim. Acta* 6, 627-40 (1923).—According to Fischer and Schrader's theory (C. A. 15, 1610) coal originated not from the cellulose of wood but from the lignin. Cellulose disappears through the action of microorganisms whereas the lignin, being more resistant, undergoes a slow disintegration into humic compds. Cellulose has been distd. *in vacuo* (C. A. 12, 2187) and the products are sol. in  $\text{H}_2\text{O}$ . P. and G. now distd. lignin (I), a by-product of the saccharification of wood, according to the Terrisse and Levy patents. I, obtained from fir wood, was freed from carbohydrates and pentosans, washed with water until the reaction was neutral and dried at  $120^\circ$ . It gave 7.8-8.0% ash and contained 14.19% MeO. It was distd. in a Cu tube at  $350-90^\circ$  under 5 mm. pressure (20 kg. during 1.5 hr.) and 15% of an oil with a green fluorescence, 21% of an acid aq. soln. and 52% of coke and ash were secured. The oil only was studied. It was dissolved in  $\text{Et}_2\text{O}$ , shaken with 10% aq. NaOH, dried over  $\text{CaCl}_2$  and freed from the solvent; the oil was 11% of the original oil and 2% of the lignin. 60% (III) of it was sol. in liquid  $\text{SO}_2$  and 40% (IV) was insol. III was boiled with Na to remove O compds. as alcs. and phenols. The fraction b.  $235-40^\circ$  contained a hydrocarbon  $\text{C}_{15}\text{H}_{16}$ , d. 0.8091,  $n$  1.4468. The fraction b.  $227-9^\circ$  contained  $\text{C}_{15}\text{H}_{16}$ , d. 0.7953,  $n$  1.4379. The fraction b.  $260-70^\circ$ ,  $\text{C}_{14}\text{H}_{16}$ , d. 0.8138,  $n$  1.4532. The fraction b.  $270-80^\circ$ ,  $\text{C}_{14}\text{H}_{16}$ , d. 0.8218,  $n$  1.4541. The fraction b.  $315-20^\circ$ ,  $\text{C}_{14}\text{H}_{16}$ , d. 0.8570. Above  $320^\circ$ , the fraction solidified into a white waxy substance, melen,  $\text{C}_{10}\text{H}_{16}$ , m.  $62-3^\circ$ . On distg. III the fraction b.  $200-10^\circ$ ,  $\text{C}_{11}\text{H}_{16}$ , d. 0.8964,  $n$  1.5119. The  $230-40^\circ$  fraction had a d. 0.9172,  $n$  1.5226. The  $250-60^\circ$  fraction,  $\text{C}_{13}\text{H}_{16}$  (?), d. 0.9372,  $n$  1.5422. The hydrocarbon  $\text{C}_{15}\text{H}_{16}$  gave a tetra-Br deriv. m.  $193^\circ$ . Of the 8 hydrocarbons from lignin and from coal in the same fractions 3 are shown to be common to each. P. and G.'s results support the F. and S. hypothesis, but the oils obtained are only 2% of the lignin and 3.5% of the coal.  $\text{H}_2\text{SO}_4$  added to the alk. soln. gave phenols which were distd. *in vacuo* and under ordinary pressure. The fractions between  $210^\circ$  and  $250^\circ$  gave all the reactions of eugenol, m.  $68^\circ$ . Benzyleugenol was prepd. An historical resumé of the facts on the nature of lignin is given. Coal has no MeO groups, lignite does contain them. Donath (Z. angew. Chem. 19, 657 (1906)) affirms therefore that lignite and coal are from different sources. However, the fossilization of vegetable matter is always accompanied by progressive loss of MeO. A table of the MeO content of several coals is given. H. E. W.



**Yeast nucleic acid. IV. A simple method for isolating adenylic acid.** H. STRUBEL AND E. PEISER. *Z. physiol. Chem.* **127**, 262-7 (1923); cf. *C. A.* **16**, 3490.—500 g. of yeast nucleic acid in 100-g. portions were dissolved in NaOH soln. and pptd. with alc. The soln. and pptn. was then repeated. The soln. of the ppt. on neutralization with AcOH gave guanylic acid (87 g. of the Na salt). The filtrates were united and pptd. with neutral Pb acetate. Pb was sepd. from the ppt. with  $H_2S$  and after concn. of the soln. it was pptd. with alc. An oil sepd. but again dissolved to a large extent. A flocculent ppt. remaining was isolated and proved to be more guanylic acid. The filtrate was pptd. with Pb acetate, the Pb was again removed and after concn. of the filtrate 57.5 g. of adenylic acid crystd.

R. L. STEHLÉ

**Chondroitinsulfuric acid.** W. SAWJALOW. *Z. physiol. Chem.* **126**, 219-49 (1923).—S. isolated from the hydrolytic products obtained from chondroitinsulfuric acid by heating 0.5 hr. with 2%  $H_2SO_4$  and subsequent benzooylation a benzoate  $C_{10}H_{10}NO_2$ ; from this he deduces the original product to be  $C_{20}H_{20}NO_4$ , to which he assigns the name *chondrin*. He believes that the formula commonly assigned to chondroitinsulfuric acid should be doubled. The benzoate of *chondroitin* is also contained in the products of benzooylation. Analysis leads to the formula  $C_{10}H_{10}NO_4$ . In the original hydrolytic mixt. is contained a substance  $(C_6H_5NO_2)_2Cu$ , giving the biuret reaction. By hydrolyzing chondroitinsulfuric acid for 2 hrs. with 10%  $H_2SO_4$  *chondrosin*,  $C_{12}H_{12}NO_4$ , is formed and may be isolated as *chondrosin phenylhydrazide*,  $C_{20}H_{18}N_2O_4$ , m.  $154^\circ$ . Chondrosin by warming at  $40^\circ$  with  $Ba(OH)_2$  forms *chitic acid*,  $C_6H_{10}O_4$ , which was isolated as the cinchonine deriv.,  $C_{20}H_{18}N_2O_4$ . From the same hydrolytic mixt. a base,  $C_7H_7N$ , was obtained as the chloroplatinate,  $(C_7H_7N)_2PtCl_6$ . R. L. S.

**Transformation of coprosterol into isolithobillanic acid.** A. WINDAUS AND TH. RIEMANN. *Z. physiol. Chem.* **126**, 277-80 (1923).—Oxidation of the di- $CO_2H$  acid  $C_{27}H_{46}O_4$  obtainable from coprosterol (*C. A.* **8**, 2398) gave isolithobillanic acid, as it should on the basis of the formulas of Windaus and Wieland for these 2 compds.

R. L. STEHLÉ

**Catalytic decomposition of anilides.** A. MAILHE. *Compt. rend.* **176**, 1718-9 (1923).—Formanilides (cf. *C. A.* **17**, 1159) on catalytic decompn. regenerate the amine; but from  $PhNHAc$  (I),  $PhNHMe$  could not be isolated. I, heated over Ni at  $400^\circ$ , yields  $NH_3$ , a gas (14%  $CO_2$ , 36%  $CO$ , 3%  $CH_4$ , 47%  $H_2$ ),  $C_6H_6$  (traces),  $PhNH_2$ , and  $(NH_4)_2CO_3$ . With very active Ni, only a gas (5%  $CO_2$ , 20%  $CO$ , 25%  $CH_4$ , 45%  $H_2$ ),  $C_6H_6$ , and  $NH_3$  are formed. Over Cu at  $410^\circ$ , it yields no  $NH_3$ , but a gas (19.5%  $CO_2$ , 13.5%  $CO$ , 67%  $H_2$ ),  $MeCN$ ,  $PhNH_2$ , and  $C_6H_6$ . Over Al, it forms  $PhNH_2$  and a gas (18%  $CO_2$ , 9%  $CO$ , 11%  $CH_4$ , 62%  $H_2$ ). *o*- and *m*-Aceto- and *o*-propionoluides react similarly. Since  $PhNMe_2$  decomp. over Al at  $400^\circ$ ,  $PhNHMe$  is probably also unstable at this temp.

I. P. ROLF

**Crystalline form of 4-chloro-2-bromo-3-nitroacetanilide.** MARIA DE ANGELIS. *Atti accad. Lincei* [v] **31**, ii, 450-3, 524-9 (1922); cf. *C. A.* **16**, 1885.—This compd. is dimorphous. The metastable  $\alpha$ -modification, d. 1.857, forms prismatic monoclinic, crystals  $a:b:c = 1.2985:1:0.5728$ ,  $\beta = 86^\circ 43'$ . The stable  $\beta$ -modification, d. 1.891, was not obtained in crystals capable of being measured accurately, but appears to be isomorphous with 2,4,3- $Br_3(O_2N)C_6H_2NHAc$ . A mixt. of 4,2,3- $ClBr(O_2N)C_6H_2NHAc$  with the di- $Br$  analog (1 mol.) yields triclinic crystals isomorphous with those of the di- $Br$  compd. A similar mixt. of 4,2,3- $ClBr(O_2N)C_6H_2NHAc$  with the di- $Cl$  compd. yields tabular, monoclinic crystals isomorphous with the  $\beta$ -form of the di- $Cl$  deriv., or, less readily, metastable, prismatic monoclinic crystals, isomorphous with those of the metastable modification of 4,2,3- $ClBr(O_2N)C_6H_2NHAc$ . J. C. S.

**Phototropism.** HANS STOBBE. *Ber. Verhandl. Sächs. Akad. Wiss. Leipzig* **74**, 161-250 (1922).—A complete list of compds. which have been studied for phototropic properties, together with literature references, is given; this includes 52 fulgides and derivs., of which 28 are phototropic, 55 fulgide acids and derivs., of which 23 are phototropic, 173 hydrazones, only 57 of which are phototropic, 34 osazones, 23 being phototropic and 242 anilines, only 19 being phototropic. The relative effect of red, yellow, green, blue and white light upon the color change for a no. of compds. is reported as well as the time for max. effect. The behavior of 13 fulgides, 15 hydrazones and 2 stilbenes is reported at  $-165^\circ$ ,  $-70^\circ$ ,  $-8^\circ$ ,  $22^\circ$ ,  $45^\circ$ ,  $75^\circ$ ,  $95^\circ$  and  $125^\circ$ . The curves for the fulgides indicate that the greatest effect is found between  $-10^\circ$  and  $40^\circ$ ; the effect falls off rapidly so that at  $125^\circ$  no change is observed, even with the strongest light sources. The "critical excitation temp.," that temp. above which no further effect is observed, is between  $40^\circ$  and  $110^\circ$ . These values are higher for the hydrazones. In order to det. whether phototropic phenomena are associated with crystal form, several compds. were mixed with resins in soln. and the solvent was removed. Of the

14 investigated fulgides, osazones and hydrazones, 7 showed normal phototropism, although in some cases a different color was observed. Crystals could not be observed under the polarization microscope. This shows that the phototropism of the substances in question is not due to crystal form but is caused by a chem. change of the material. These plastic masses as well as the mixed crystals or solid solns. of Padoa are to be considered as intermediate steps between the individual phototropic crystals and non-phototropic liquid solns. Ketones, on the other hand, do not show this phenomenon and their phototropism must be connected with their cryst. form. It is further shown that the phenomena persist when the dyes are present in fibers (wool, cotton, silk), although the effect is not as pronounced. This may be explained by the formation of a chem. compd. with the fiber or by adsorption upon the fiber. The effect of a vacuum,  $\text{CO}_2$ , O, and H upon the phototropic properties showed that there was no regularity in the case of the various compds. In the case of stilbene derivs. the color changes are probably oxidation-reduction processes. The heat of combustion of the orange triphenylfulgide A is 7810.4 cal., that of the light form B, 7816.9 cal. C. J. WEST

**Destructive action of nitric acid upon phenols.** MOROZ IWATA. *J. Chem. Soc. Japan* 44, 391-406(1923).—By adding 60%  $\text{HNO}_3$  in drops to recrystd. gallic acid, m.  $220^\circ$ . I. obtained  $\text{CO}_2$ , HCN, and  $\text{H}_2\text{C}_2\text{O}_4$  but no AcOH. The yield of HCN from different amts. of gallic acid with the same amt. of  $\text{HNO}_3$  (20 cc. of 60% acid) were: 1-1.04% (of gallic acid) with 0.5 g.; 0.87-1.85% with 1 g.; 1.50-1.86% with 3 g.; and 0.79% with 4 g. With diln. of the  $\text{HNO}_3$  the yield of HCN is lowered. The yield of  $\text{H}_2\text{C}_2\text{O}_4$  which comes down in cryst. form, m.  $100^\circ$ , during the reaction, is on the average 45%. Thus 1 mol. of gallic acid gives approx. 1 mol. of  $\text{H}_2\text{C}_2\text{O}_4$  (8% loss). In the decompn. products, no phenols could be detected. All the other phenols gave similar products with  $\text{HNO}_3$ . The min. concns. of  $\text{HNO}_3$  which will decomp. the different phenols and their derivs. at room temp. and when heated, resp., are as follows: gallic acid 30, 8%; protocatechuic acid 30, 1.5-2; salicylic acid, no action even with concd. acid, 8.1; pyrogallie acid 30, 20; phloroglucinol —, 15; resorcinol —, 15; hydroquinol 30, 15; guaiacol 30, 8; PhOH 50 (nitration also occurs); 8.1; thymol, concd., concd.; PhMe and  $\text{C}_6\text{H}_5$  no decompn.; kaki tannin (one of the gallotannins), —, 30;  $\text{C}_6\text{H}_5$  —, —; and  $\alpha$ -naphthol and  $\beta$ -naphthol forms HCN with hot  $\text{HNO}_3$ , but no  $\text{H}_2\text{C}_2\text{O}_4$ . HCN and  $\text{H}_2\text{C}_2\text{O}_4$  found in plants might have come from phenols. S. T.

**Acetylation with acetic anhydride and sulfuric acid.** O. FERNÁNDEZ AND C. TORRES. *Anales soc. españ. fis. quim.* 21, 22-32(1923).—Salicylic acid, morphine, and a no. of phenols were completely acetylated by mixing with an excess of  $\text{Ac}_2\text{O}$  at room temp. and adding 1 or 2 drops of concd.  $\text{H}_2\text{SO}_4$  to start the reaction. No heating is needed other than that produced by the reaction itself. Cf. C. A. 15, 1869.

L. E. GILSON

**Monomethyl orthophosphosalicylic acid ester.** ÉMILE GAUTRELET. *Compt. rend.* 176, 1770-2(1923).—Two isomers exist as shown by the formulas I and II in the following reaction:  $3\text{MeH}_2\text{PO}_4 + 3\text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{Na} \longrightarrow \text{Na}_3\text{PO}_4 + \text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{Me} + \text{HO}_2\text{CC}_6\text{H}_4\text{OPO}(\text{OH})\text{OMe}$  (I) +  $\text{HOC}_6\text{H}_4\text{CO}_2\text{PO}(\text{OH})\text{OMe}$  (II) +  $2\text{H}_2\text{O}$ . The proportions in which I and II are formed depends on the temp. of the reaction, high temp. favoring the production of I. Both form colorless orthorhombic crystals, those of I being short and thick, those of II being needles. I m.  $113^\circ$ , II  $98^\circ$ . The violet color reaction with  $\text{FeCl}_3$  is less sharp with I than with II. The physiol. actions of I and II appear to be identical. L. W. RIGGS

**Molecular weight of benzaldehyde-copper and the formation of benzaldehyde-copper-pyridine.** FRITZ SCHAAP. *Helvetica Chim. Acta* 6, 535-8(1923); cf. C. A. 17, 2664.—Mol. wt. detns. of benzaldehyde-Cu in camphor (f. p. depression) show that it is monomol. The  $d_4$  is 1.4552. A soln. of the Cu deriv. in  $\text{C}_6\text{H}_5\text{N}$  deposits benzaldehyde-copper-pyridine,  $2\text{C}_{14}\text{H}_{12}\text{O}_2\text{Cu} \cdot 5\text{C}_5\text{H}_5\text{N}$ , deep blue needles, which loses  $\text{C}_6\text{H}_5\text{N}$  when heated to  $150^\circ$  or when treated with NaOH or dil. acids. The prepn. and decompn. of this compd. are a suitable method for purification of the Cu deriv. Other bases likewise dissolve the Cu deriv. and probably yield derivs. similar to the  $\text{C}_6\text{H}_5\text{N}$  deriv. C. J. WEST

**Action of bases on  $\alpha,\alpha,\beta$ - and  $\alpha,\beta,\beta$ -tribromo- $\beta$ -phenylpropionic acids and their esters.** P. R. AYYAR AND J. J. SUDBOROUGH. *J. Indian Inst. Sci.* 6, 69-92(1923).—The elimination of  $\text{CO}_2$  from  $\text{PhCHBrCBr}_2\text{CO}_2\text{H}$  (I) by boiling with  $\text{H}_2\text{O}$  proceeds almost quant. according to the equation:  $\text{I} = \text{PhCBr} : \text{CHBr} + \text{HBr} + \text{CO}_2$ , 92% of the  $\text{CO}_2$  being recovered by absorption with KOH. The compn. of mixts. of *cis*- and *trans*- $\text{PhCBr} : \text{CBrCO}_2\text{H}$  is most conveniently detd. by sepn. of the Na salts by means of NaCl solns. in which the salt of the *cis* acid is readily sol. The best conditions are a concn. of NaCl of 16-20%, that of the Na salts of the acids 10% and the temp.  $25^\circ$ . NaOH

or KOH in EtOH eliminates HBr from I or  $\text{PhCBr}_2\text{CHBrCO}_2\text{H}$  (II), giving a mixt. of the two  $\text{PhCBr}_2\text{CHBrCO}_2\text{H}$  (III). The reaction is complicated by the readiness with which  $\text{CO}_2$  is also eliminated; this reaction is favored by replacement of EtOH by  $\text{H}_2\text{O}$ , by using a dil. soln. of alkali and by comparatively high temp. By stirring for 18-24 hrs. at  $50^\circ$  or by shaking 92 hrs. at  $25^\circ$ , it is possible in the case of I to obtain an 80% yield of III and from II a 90% yield is obtained at  $-5^\circ$  to  $15^\circ$ . Similar reactions take place when the esters are shaken with an alc. soln. of 2-2.5 equiv. of alkali. Thus HBr is more readily eliminated from II and its ester than from I and its ester. The relative proportions of *cis*- and *trans*-acids is not appreciably affected by replacement of alc. KOH by alc. NaOH or by substituting the ester for the free acid. With I and its ester and KOH the ratio of *cis*- and *trans*-acid is 1:3, whereas with II or its ester the ratio is 1:1.4. If  $\text{CO}_2$  is also split off the ratio can fall to 1:9 or even 1:12. The action of  $\text{PhNMe}_2$  with  $\text{PhCBr}_2\text{CHBrCO}_2\text{H}$  proceeds in 2 directions: the 1st gives  $\text{PhCH:CHBr}$ ,  $\text{CO}_2$  and  $\text{PhNMe}_2\text{HBr}$ ; the 2nd,  $\text{PhCH:CHCO}_2\text{H}$ ,  $\text{BrC}_6\text{H}_4\text{NMe}_2$  and HBr. About 20% of the acid reacts according to the 1st equation. With I and II the reaction is mainly of the type of the 1st reaction. The products are chiefly  $\text{PhCBr}_2\text{CHBr}$ ,  $\text{CO}_2$  and HBr. Small amts. of acids are also formed but the mixt. is oily and appears to be a mixt. of the Br and Br<sub>2</sub> acids. With the esters, on the other hand, the main reaction consists in the elimination of Br from the esters and the production of  $\text{BrC}_6\text{H}_4\text{NMe}_2$ . To a small extent there is also a reaction analogous to that with alc. KOH, so that the ester formed is a mixt. Other org. bases such as  $\text{PhNH}_2$  and  $\text{C}_6\text{H}_5\text{N}$  appear to behave in a manner exactly similar to  $\text{PhNMe}_2$ . C. J. WISE

**Condensation of nitriles with thioamides.** II. Acetonitrile with thiobenzamide and benzonitrile with thioacetamide. SEIICHI ISHIKAWA. *J. Chem. Soc. Japan* **44**, 382-91(1923); cf. C. A. **16**, 1588, 3884.—In Paper I, I. obtained benziminoisothioibenzamide (IV) by passing HCl into PhCN (I) and thiobenzamide  $\text{PhC(SH):NH}$  (II), in  $\text{Et}_2\text{O:C(SH)Ph}$  (IV). If MeCN (III), condenses with II in a similar manner, the product should be acetimino isothioibenzamide,  $\text{MeC(:NH)N:C(SH)Ph}$ . The product, however, formed red crystals, m.  $75^\circ$ . After the possible presence of I as an impurity had been eliminated, it was concluded that either I must be produced from II by the action of HCl, or must be a product of reaction between III and II. If I were formed from II, passing HCl into II alone in  $\text{Et}_2\text{O}$  should produce IV because I thus formed from II can act with the unchanged II. The results were negative. As soon as III was added, however, IV was formed. Therefore, the reaction between II and III must go on as follows.  $\text{MeCN} + \text{HN:C(SH)Ph} = \text{MeC(:NH)N:C(SH)Ph} + \text{MeC(:NH)N:C(SH)Ph} = \text{MeC(:NH)SH} + \text{PhCN}$ .  $\text{PhCN} + \text{HN:C(SH)Ph} = \text{PhC(:NH)N:C(SH)Ph}$ . The correctness of this hypothesis was confirmed by identifying thioacetamide (V) as intermediary product. The yield of IV from II and III is at best 14% of the II used, while a quant. yield can be obtained from I and II. When I and V are treated in this way, IV and a large amt. of II (71%) are obtained. The reaction,  $\text{PhCN} + \text{MeC(:NH)SH} \rightleftharpoons \text{PhC(:NH)SH} + \text{MeCN}$  reaches equil. at an 80:20 ratio. This fact is considered to be the reason why the yield of IV from II and III is so small. S. T.

**Constitution of some imidosulfides.** H. RIVIER AND J. SCHALCH. *Helvetica Chim. Acta* **6**, 605-17(1923).—Continuation of C. A. **14**, 1301. May (C. A. **8**, 1266) reported on  $\text{PhC(NPh)SMe}$  and  $\text{PhCSNPhMe}$ . These compds. are decompd. easily by heat without transformation into their isomers. R. and S. studied the compds. resulting when Me is replaced by Ph.  $\text{PhCSNPhPh}$  (IV) (prepd. by treating  $\text{BzNHPh}$  in boiling  $\text{C}_6\text{H}_6$  with  $\text{P}_2\text{S}_5$ ) and  $\text{BzCl}$  in  $\text{C}_6\text{H}_6$  were allowed to stand with 2N NaOEt, then warmed slightly, filtered and evapd. The residue was *S*-benzylthiobenzanilide (I). I in  $\text{Et}_2\text{O}$  with HCl gave a yellow cryst. *HCl salt*, m.  $131-2^\circ$  (decompn.), giving I.  $\text{H}_2\text{O}$  decomp. the compd. Fleisher's method (*Ann.* **138**, 225(1866)) for prep.  $\text{PhNHCH}_2\text{Ph}$  was modified as follows: The reaction between  $\text{BzCl}$  and NaOEt, which is attended with evolution of heat, was finished by heating to  $120-50^\circ$  for 20 min. The mixt. was taken up in  $\text{C}_6\text{H}_6$ , freed from  $\text{PhNH}_2\text{HCl}$  by agitating with  $\text{H}_2\text{O}$ , dried, decolorized with bone black and benzoylated by the Schotten-Baumann reaction, using  $\text{Na}_2\text{CO}_3$ , yielding  $\text{PhNBzCH}_2\text{Ph}$  (II), m.  $104^\circ$ . The product is better than when prepd. by the Fleisher method. II boiled several min. in  $\text{CS}_2$  with  $\text{P}_2\text{S}_5$ , filtered and evapd., gave a viscous mass which in  $\text{C}_6\text{H}_6$  or  $\text{CHCl}_3$  was decolorized. The resulting *N*-benzylthiobenzanilide, m.  $121-2^\circ$ , does not add HCl.  $\text{H}_2\text{SO}_4$  decomp. it with formation of  $\text{BzNHPh}$ . Dithiodiacylanilides (imidoxanthides) were prepd. by the action of an imidochloride on an alk. xanthate, by the action of an ester of  $\text{ClCSOH}$  on Na thioanilide and by the action of  $\text{ClC(:NPh)OEt}$  on  $(\text{PhCS}_2)_2\text{Ph}$ .  $\text{PhCSNPhCSOEt}$  (Chugaev, *Ber.* **35**, 2470(1902)) m.  $98.5^\circ$ , is shown by R. and S. to exist in 2 forms,

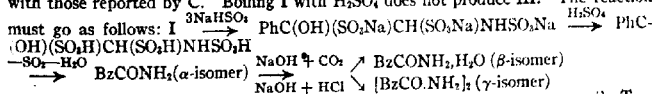
one garnet-red and other bright red. The latter results when the former is crystd. in alc. and  $H_2O$ . The transformation is quant. at  $80^\circ$ . They have the same mol. wt.  $\alpha$ - $PhCCl_2NC_6H_5$  and  $EtOCS_2K$  in 20 min. gave *Et*  $\alpha$ -thiobenznaphthalidethionecarbonate, m.  $142^\circ$ . The  $\beta$ -form prepd. under the same conditions m.  $123-4^\circ$ .  $EtOCSCl$  (III) (Delépine, *C. A.* 6, 83) may be prepd. by letting  $NaOEt$  stand with  $CSCl_2$  in  $CHCl_3$  3 hrs., agitating with  $H_2O$ , drying carefully and distg. The yellow liquid b.  $126-7^\circ$ . When III is warmed in  $C_6H_6$  or  $CHCl_3$  with  $NaOEt$  several min. on the water bath, freed from  $NaCl$  with  $H_2O$ , dried with  $CaCl_2$  and treated with abs. alc. or petr. ether, **V** results. *Ph* thiobenzanilidethionecarbonate, prepd. from  $PhOCSCl$  and **IV** in the presence of soda, m.  $112-3^\circ$ , does not combine with  $HCl$ , dissolves in  $H_2SO_4$  with red color and slow decompn. **IV** is found among the decompn. products. *Ph* *p*-dimethylaminothiobenzanilidethionecarbonate, similarly prepd. from  $PhOCSCl$  with dimethylaminothiobenzanilide (Rivier and Schneider, *C. A.* 14, 744), m.  $121-2^\circ$ , decompn. slowly and dyes silk in dil.  $HOAc$  soln. because of the  $-NMe_2$  group.  $HCl$  when passed through the  $Et_2O$  soln. gave a *HCl* salt. *Ph*  $\beta$ -thiobenznaphthalidethionecarbonate, prepd. by gently heating  $PhOCSCl$  with  $\beta$ - $PhCSNHCl$ , (Rivier and Schneider, *C. A.* 14, 1301) in the presence of alc. soda, m.  $145-6^\circ$  and decompn. readily.  $\beta$ -Naphthyl chlorothionecarbonate,  $\beta$ - $C_{10}H_7OCSCl$ , prepd. by warming  $C_{10}H_7ONa$  and  $CSCl_2$  gently on the water bath for 10-5 min., yellow crystals, m.  $76-7^\circ$ . When warmed to boiling in alc. it gave *Et*  $\beta$ -naphthylthiocarbonate, m.  $67^\circ$ .  $\alpha$ -Naphthyl chlorothionecarbonate is much less stable than the  $\beta$ -compd. and its prepn. is more difficult. It b.  $165-6^\circ$ .  $CSCl_2$  in  $C_6H_6$  and  $\alpha$ - $C_{10}H_7ONa$  give a red viscous mass which must be distd. *in vacuo*.  $\beta$ -Naphthyl thiobenzanilidethionecarbonate, prepd. like the *Ph* deriv., red-brown, m.  $131-2^\circ$ .  $\beta$ -Naphthyl  $\beta$ -thiobenznaphthalidethionecarbonate (**VII**), red-brown crystals, m.  $163-4^\circ$ .  $\beta$ -Naphthyl  $\alpha$ -thiobenznaphthalidethionecarbonate, m.  $133^\circ$  and is more stable than **VII**.  $\alpha$ -Naphthyl  $\beta$ -thiobenznaphthalidethionecarbonate, m.  $134-5^\circ$ , was also prepd. The action between  $(PhCS)_2Pb$  (Houben, *Ber.* 39, 3224 (1906)) and  $EtOC(NPh)Cl$  in  $C_6H_6$  or  $CHCl_3$  is slow in the cold and is complete only after 2 or 3 months. The action of  $(PhCS)_2Pb$  on  $PhOC(NPh)Cl$  is also slow but should be effected at ordinary temp. because of decompn. **P** and **S** attempted to prep. analogous dithiodiacylanilides but without success. When  $PhOCSCl$  was treated with  $PhCSNHPh$ ,  $PhCSNHCSOPh$  was not formed but other products, among them  $CS(OPh)_2$  and  $PhCN$ .

H. E. W.

**A simple preparation of pyromellitic acid.** HENRI DE DIERSBACH, VICTOR SCHMIDT and EUGENE DECKER. *Helvetica Chim. Acta* 6, 548-9 (1923).—Impure xylene when brominated gives a mixt. of bromoxylenes, which give a mixt. of the dinitriles of  $\alpha$ - and  $\beta$ -cumidinic acids. These nitriles are sapon. with 70%  $H_2SO_4$ , giving a mixt. of the two acids which can be oxidized by  $KMnO_4$  in the cold to pyromellitic acid. The yield by oxidation is about 90%.

R. CHESTER ROBERTS

**Beckmann transformation of nitrosoketones.** SHINTARO KODAMA. *J. Chem. Soc. Japan* 44, 339-52 (1923).—The Beckmann transformation of  $PhCOCH_2NOH$  (**I**) is shown here to occur in the presence of  $H_2O$ . **I**, prepd. by the method of Claisen and Manasse (*Ber.* 20, 2194), forms yellow needles, m.  $126-8^\circ$ . With excess of **I** (10 g.) and  $NaHSO_3$  (15 g. of satd. soln.) was obtained  $C_6H_5NO_2 \cdot 2NaHSO_3$  (**II**), and with excess of  $NaHSO_3$  (4-5 vols. of satd. soln. to 1 part of **I**),  $C_6H_5NO_2 \cdot 3NaHSO_3$ . When 2.3 g. of **II** in 20 cc. 20%  $H_2SO_4$  is cooled after heating 1 min., 0.5772 g. of needles m.  $90-1^\circ$  and having the compn.  $C_6H_5NO_2$  (**III**) is obtained. From  $C_6H_5NO_2 \cdot 3NaHSO_3$ , the same product can be obtained. That **III** is  $BzCONH_2$  is shown in the following tests. On treating **III** with alkali  $NH_3$  and  $OHCCO_2H$  split off easily. Since the properties of **III** are very similar to those of the  $\alpha$ -isomer of  $BzCONH_2$  obtained by hydrolysis of  $BzCN$  (Claisen), K. prepd. the  $\beta$ - and  $\gamma$ -isomers from **III** ( $\beta$ -isomer,  $C_6H_5NO_2 \cdot H_2O$ , m. about  $60^\circ$ ;  $\gamma$ -isomer,  $[C_6H_5NO_2]_2$ , m.  $134-5^\circ$ ) and found these to be exactly identical with those reported by C. Boiling **I** with  $H_2SO_4$  does not produce **III**. The reaction



S. T.

**Alleged phenylglyoxal.** SHINTARO KODAMA. *J. Chem. Soc. Japan* 44, 353-69 (1923).—Pechmann (*Ber.* 20, 2904), first gave the method of prepn. of  $BzCHO$ , whose hydrate is reported to form needles, m.  $73^\circ$  (Pinner gives  $91^\circ$ ). In Beckmann's rearrangement of  $PhCOMe$  (see preceding abstr.), in which the treatment is similar to P.'s method of prepn. of  $BzCHO$ , K. obtained  $BzCONH_2$ , the properties of which are

identical with those of P.'s  $\text{BzCHO}$ . The so-called "phenylglyoxal" subsequently reported in the literature is really  $\text{BzCONH}_2$ . The fact that the  $\text{NaHSO}_3$  salt of  $\text{PhCOCH:NOH}$  gives derivs. of  $\text{BzCHO}$  is due to rearrangement of the  $\text{PhCOCH:NOH}$ . Miller and P. (*Ber.* 22, 2556) also give this method for prep. tolylglyoxal,  $p\text{-MeC}_6\text{H}_4\text{COCHO.H}_2\text{O}$ , m. 95-102°; its hydrazone,  $\text{MeC}_6\text{H}_4\text{C( : N.NH.Ph)CH : N.NHPh}$ , m. 145°. According to K.,  $p\text{-MeC}_6\text{H}_4\text{COCH:NOH}$  m. 101-1.5°, and its  $\text{NaHSO}_3$  salt has the compn.  $\text{C}_9\text{H}_7\text{O}_2\text{N.2NaHSO}_3$ . When boiled with 17%  $\text{H}_2\text{SO}_4$  it gives  $\text{C}_9\text{H}_7\text{O}_2\text{N}$  (I), m. 118°. When I is boiled with alkali,  $\text{NH}_3$  and  $\text{MeC}_6\text{H}_4\text{COCO}_2\text{H}$  are formed, and the so-called "tolylglyoxal" must be tolyl formamide. Claus and Krosberg (*Ber.* 20, 2050), synthesized I by a different method and give the m. p. 160°, different from K.'s. Since C. and K. only detd. its compn.,  $\text{C}_9\text{H}_7\text{O}_2\text{N}$ , and its m. p. is similar to that of  $\text{MeC}_6\text{H}_4\text{COCOCONH}_2$  (m. 159-60°), their product might have been the amide. The phenylhydrazone of I,  $\text{MeC}_6\text{H}_4\text{C( : N.NH.Ph)CONH}_2$ , m. 159°, and ozazone m. 119-20°. In a study the chemistry of aldehydes (*C. A.* 17, 2571) K. prepd. according to P.'s method the compd. which is in reality  $\text{BzCONH}_2$ , not  $\text{BzCHO}$ . S. T.

**Beckmann rearrangement of oximes to amides.** ERNST BECKMANN and ERICH BARR. *J. prakt. Chem.* 105, 327-49(1923); cf. *C. A.* 17, 1218.—Concd.  $\text{H}_2\text{SO}_4$  and dimethylchromone oxime react to give a *sulfonic acid*, analyzed as the *Ag salt*,  $\text{C}_{11}\text{H}_{11}\text{NO}_5\text{S.Ag}$ , sensitive to light. The oxime is not changed by  $\text{PCl}_5$ ,  $\text{HCl}$ ,  $\text{AcCl}$ ,  $\text{AcOH}$  or  $\text{Ac}_2\text{O}$ . It is not possible to remove the oxime group by means of heating with  $\text{H}_2\text{SO}_4$ ,  $\text{NaOH}$ ,  $\text{HCHO}$ ,  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  or to prep. the semicarbazone or phenylhydrazone of dimethylchromone. The CO group does not possess the normal functions of a ketone. This explains why in the reaction of dimethylchromone and  $\text{NH}_2\text{OH}$  a NO deriv. and not an oxime is formed. 2,3-Dimethyl-1-thiochromone forms a true oxime, but because of the presence of the bridge S the compd. is very sensitive and a rearrangement product could not be obtained. A smear is formed upon addn. of the rearranging substances. Isatin oxime is not affected by  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{AcCl}$  or  $\text{Ac}_2\text{O}$ . A mixt. of  $\text{PCl}_5$  and  $\text{POCl}_3$  gives  $o\text{-NCC}_6\text{H}_4\text{NCO}$ .  $\text{PhSO}_2\text{Cl}$  reacts to give a *sulfonic acid deriv.* (I),  $\text{C}_8\text{H}_5\text{O}_4\text{N}_2\text{S}$ , m. 130-1°. Attempts to split off the Ac group from acetylisingindioxime failed. Weak bases ( $\text{C}_6\text{H}_5\text{N}$  and  $\text{C}_6\text{H}_7\text{N}$ ) had no action while stronger bases (KOH) split off an oxime group also.  $\text{PhSO}_2\text{Cl}$  in  $\text{C}_6\text{H}_5\text{N}$  gave I.  $\text{BzCl}$  in  $\text{NaOH}$  gave a Bz deriv. of isatin oxime. In the case of  $\text{Ph}_2\text{C:NOH}$ , the Beckmann rearrangement may be brought about by the use of  $\text{MgCl}_2$ ,  $\text{KCl}$ ,  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{HgCl}_2$ ,  $\text{HgCl}$ ,  $\text{HgCl}_2$ ,  $\text{SbCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{POCl}_3$ , in some cases the yield being quant. The best action occurs with  $\text{SbCl}_5$  in  $\text{CHCl}_3$  in the cold.  $\text{NH}_4\text{Cl}$  and  $\text{COCl}_2$  regenerate the ketone as does heating with mol. amts. of  $\text{CaO}$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{HgO}$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , etc. Cryst.  $\text{ZnSO}_4$  has no action on the oxime at 165°, while the anhydrous salt regenerates the ketone. The anilide, once formed, is more stable than the oxime.  $\text{COCl}_2$  and  $\text{HgO}$ , which decomp. the oxime to the ketone, do not affect the anilide. In how far these new rearranging agents may be applied to other oximes must be investigated. C. J. WEST

**Isatogens. IV. Addition products of isatogens.** P. RUGGLI, A. BOLLIGER and W. LEONHARDT. *Helvetica Chim. Acta* 6, 594-604(1923); cf. *C. A.* 16, 84.—When 6-nitro-2-phenylisatogen (I) is heated about 3 hrs. with very pure  $\text{AcCl}$ , an orange-yellow to yellow soln. is obtained from which, upon evapn., there seps. the *AcCl addn. product*, yellow, decomp. 145-60°; in the dry state it may be kept up to 2 weeks. In  $\text{CHCl}_3$  it is immediately decompd. by  $\text{PhNH}_2$  or  $\text{PhNHNH}_2$ , giving I. If the  $\text{AcCl}$  soln. is poured upon ice, the *AcOH addn. product* results as yellow needles, decomp. 125°. It is quant. decompd. by boiling  $\text{EtOH}$ , and has no oxidizing properties towards  $\text{NaI-AcMe}$  soln. With  $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$  in boiling  $\text{C}_6\text{H}_6$ , the Cl group is replaced by  $\text{O}_2\text{NC}_6\text{H}_4\text{NH}$ , giving a sandy yellow powder, m. 214°.  $\text{MeOH}$  gives the *MeO deriv.*, yellow, m. 164.5°. *EtO deriv.*, m. 144.5-5°, decomp. 170°. *AcO addn. product*, yellow, m. 193-5° (decompn.); it is decompd. by heating with  $\text{AcOH}$  or dil.  $\text{EtOH-K}_2\text{CO}_3$ . Shaken with  $\text{EtOH-HCl}$  in the sunlight, there results an *EtOH addn. product*, brownish yellow, splitting off  $\text{EtOH}$  at 80-90°. Additional details of the prep. of isonitrophenylisatogen (*C. A.* 13, 1473) are given. C. J. WASS

The oxidation of 1,3,4-dimethylcyclohexanone and the synthesis of cyclopentane diketones. MARCEL GODCHOT. *Bull. soc. chim.* 133, 963-9(1923).—See *C. A.* 17, 2280. E. J. C.

**Japanese bird lime. III.** H. YANAGISAWA and N. TAKASHIMA. *J. Pharm. Soc. Japan* 494, 251-8(1923).—In order to det. the nature of the OH group of trochol,  $\text{C}_{20}\text{H}_{34}\text{O}$ , prepd. from the Japanese bird lime, *Trochodendra cratioides* (cf. *C. A.* 16, 795, 1937), various derivs. of trochol were prepd. and their chem. compn. and phys. properties are recorded. The results are: phenylcarbamate,  $\text{C}_{20}\text{H}_{34}\text{O}_2(\text{PhNHCO})$ , m. 167°; formate,  $\text{C}_{20}\text{H}_{34}\text{O}_2(\text{OCH})$ , m. 306°; phthalate,  $\text{C}_{22}\text{H}_{36}\text{O}_4(\text{OCC}_6\text{H}_4\text{CO}_2\text{H})$ , m. 205°;

semicarbazone,  $C_{28}H_{40}O_7$ ;  $NNHCONH_2$ ; m.  $290^\circ$ ; oxime,  $C_{28}H_{40}O_7$ ;  $NOH$ , m.  $217^\circ$ ; and dihydroxycarboxylic acid (trocholic acid),  $C_{28}H_{40}O_8$ , m.  $282^\circ$ ; Ac deriv. of trocholic acid  $C_{28}H_{40}O_8Ac$ , m.  $145^\circ$ . The conclusion is that two O atoms of trochol exist as a secondary and a tertiary OH. When especially carefully dried trochol is mixed with abs.  $CHCl_3$  and moistened with a little  $H_2O$ , vigorous oxidation occurs, giving off a  $PrCo_2H$  odor; if distd. with steam,  $AcOH$  is formed. The method of prepn. of these derivs. and analytical data, together with various properties, such as cryst. forms, are given in detail.

S. T.

**Constituents of derris root.** T. KARIYONE AND K. ATSUMI. *J. Pharm. Soc. Japan* 491, 10-7(1923).—Toeba, the root of *Derris elliptica*, Benth, is used to paralyze fishes, and its powder or ext. was recently introduced as an insecticide. The chem. nature of tubotoxin (I), first isolated by Ishikawa, from the root is reported here. 6.65% crude I was obtained by I.'s method. It crystd. from alc. in crystals, m.  $163^\circ$ , and has the compn.  $C_{18}H_{19}O_8$ . To study the nature of the O, I was treated with  $PhNHNH_2$  and glacial  $AcOH$  on the water bath (2 hrs.). Yellow needles,  $C_{17}H_{19}O_8C:NNHPh$ , m.  $255^\circ$ , were obtained. Since the oxime, m.  $245^\circ$ , has also the compn.  $C_{17}H_{19}O_8C:NOH$ , I must have 1 carbonyl group. When I was heated with an equal amt. of anhyd.  $NaOAc$  and 5 parts of glacial  $AcOH$  for 2 hrs. at  $140^\circ$  it gave "diacetyl tubotoxin" (?), needles, whose m. p. is not definite, and sapon. no. is lower than the calcd. Although the formation of the "di-Ac" deriv. is doubtful, I has the power to utilize some alkali. With  $BzCl$ , no Bz deriv., with phthalic anhydride, none of its ester was formed. Dett. of MeO gave 1.5 with  $AgNO_3$ , and 1.11 with  $PhNMe_2$ . Since tubotoxin and rotenone have similar properties (rotenone,  $C_{18}H_{19}O_8$ , m.  $163^\circ$ ; phenylhydrazone m.  $243^\circ$ ), they are possibly identical. Tables are given to compare the properties of tubotoxin, rotenone, pachyrhizide and timboin, in respect to crystal form, m. p., compn., mol. wt., and m. p. of the phenylhydrazones.

S. T.

**Derivatives of buccocamphor.** Y. ASAHINA AND S. KUWADA. *J. Pharm. Soc. Japan* 491, 1-9(1923).—Since certain properties of derivs. of buccocamphor (I) reported by A. and Mituhori (*C. A.* 16, 2502) differ from those on record, A. and K. reinvestigate them. I was prepd. by A. and M.'s method of oxidation of menthone by  $FeCl_3$  (12 g. from 50 g. menthone, which must be pure in order to obtain cryst. I). A. and K. confirm the m. p. of the phenylurethan ( $113^\circ$ ), and could not obtain  $41^\circ$ , as Semmler and MacKenzie report (*Ber.* 39, 1169). Kondakow and Bjab-obrzeski (*J. prakt. Chem.* [2] 54, 437), give  $156^\circ$  for the m. p. of the oxime, and S. and M.  $125^\circ$ , while A. and M. could not obtain a cryst. oxime. In repeating the reaction again, A. and K. boiled alc.  $NH_4OH$  and I under a reflux condenser on a water bath for 5 hrs. and obtained a cryst. compd. m.  $123^\circ$ , whose N content corresponds to a mon-oxime and which gives a green color with  $FeCl_3$ ; it probably corresponds to the oxime of S. and M. On boiling for 10 hrs., however, A. and K. obtained a compd. m.  $154-7^\circ$  (m. p. not sharp), which is a dioxime. If I is heated with  $NH_4OH.HCl + NaOAc$  in alc. in a sealed tube at  $100^\circ$  for 10 hrs. an oil and a cryst. substance, m.  $192^\circ$ , are obtained, the latter being a dioxime, which does not give a color reaction with  $FeCl_3$ . The different m. ps. of the dioxime must be due to the existence of isomers.  $C_{10}H_{14}O_4$  (II) was obtained by S. and M. by oxidizing I in  $Me_2CO$  with  $KMnO_4$ , and they assumed that during this oxidation, an intermediate compd.  $C_{10}H_{14}O_4$  (III) must be formed. A. and M. previously isolated a cryst. compd. m.  $129^\circ$  which had the same compn. as III and considered it to be the intermediary compd. of S. and M. In repeating this oxidation, A. and K. could not obtain the same compd. and instead, obtained a sirupy compd. and sometimes a cryst. substance m.  $44.5^\circ$  (semicarbazone  $157^\circ$ ) which is  $\alpha$ -isopropyl- $\gamma$ -acetyllactic acid, the same product obtained by S. and M. by oxidation of I by  $O_3$ . In oxidizing I by alk.  $KMnO_4$ , however, III, m.  $135^\circ$ , was easily obtained. III easily loses  $H_2O$  and goes to II, m.  $104-5^\circ$ , even by distn. or slightly heating with  $HCl$ . When III is treated with semicarbazide,  $PhNHNH_2$ , or  $NH_4OH$ , the resulting condensation products are not derivs. of III, but of II.

S. T.

**New investigations in the field of sesquiterpenes and diterpenes.** F. KLINGEMANN. *Z. angew. Chem.* 36, 317-23(1923).—While the constitution of the terpenes is known for most of the representatives of this class and even the relation of one to another, the constitution of only one of the 300 sesquiterpenes which have been isolated is known with any certainty. This article is a theoretical discussion of the constitution and interrelation of the members of this group, illustrated by many formulas, which are necessary to convey the ideas expressed. No exptl. work is given.

C. J. WEST

**Higher terpene compounds. X. Isomerism in the resin acids of the abietic acid group.** L. RŮŽICKÁ AND H. SCHINZ. *Helvetica Chim. Acta* 6, 692-73(1923); cf. *C. A.* 17, 2419.—The abietic acid normally present in rosin is d-rotatory; heating to

250° for the action of mineral acids transforms this into a *l*-acid, practically identical with that obtained by Steele (C. A. 16, 2324) through the action of AcOH; further heating (300°) again transforms it into a *d*-acid. Several examples are given with numerical values. The *l*-acid crystals easily. The acids from French resins show the same behavior. Unlike the American resin, the French resin may be distilled at 12 mm. without splitting off CO<sub>2</sub>, 75% of the product b. 245–55°, m. (not sharply) 180° and having  $[\alpha]_D -60$  to  $-70^\circ$ . Crystd. 3 times from AcMe the acid m. 159–81°,  $[\alpha]_D -50^\circ$  (5% EtOH). Heated to 300° for 24 hrs. (CO<sub>2</sub> atm.) the acid m. 180–3° and has  $[\alpha]_D 55^\circ$  (3% EtOH); the corresponding American acid under the same conditions m. 170–9°,  $[\alpha]_D 46^\circ$ . A sample of acid which had not been heated above 60° during its isolation was crystd. 3 times from AcMe, m. 142–3°,  $[\alpha]_D -138^\circ$  (5% EtOH) and consisted of rectangular tablets. This is more readily reduced by H and Pt black to tetrahydroabietic acid, m. 168–70°, 19° (4.5% EtOH). The original acid therefore contains 2 double bonds. It is isomerized by boiling with AcOH for 2 hrs., giving an acid m. 162–4°  $[\alpha]_D -92^\circ$ ; it forms monoclinic crystals, *a*(100), *u*(110), *w*(111), *o*(111), *o'*( $\bar{1}\bar{1}\bar{1}$ ), *p*( $\bar{1}\bar{1}\bar{1}$ ), *p'*( $\bar{1}\bar{1}\bar{1}$ ), *c*(001), *c'*(001), *a*: *u*, 47° 41', *a*: *c*, 47° 38', *a'*: *w'*, 70° 39'. This is practically identical with the acid distd. in a high vacuum and m. 158°. The abietic acid group thus consists of tricyclic compds. contg. 2 double bonds. **XI. *d*-Pimaric acid and the distribution of resin acids.** L. RUZICKA and Fr. BALAS. *Ibid* 677–91.—Digestion of 25 kg. galipot 4 times with an equal amt. of 75% EtOH and crystn. from 80% EtOH gave 6.5 kg. mixed acids, m. about 130° and  $[\alpha]_D -70^\circ$ . A further crystn., transformation into the Na salt and crystn. of this salt 5 times from H<sub>2</sub>O at 60° gave 2.5 kg. Na salt, from which 1.9 kg. pimaric acid, m. 160–75°,  $[\alpha]_D -86^\circ$ , were obtained by passing CO<sub>2</sub> into the aq. soln. at 60°. Crystn. from 10 l. AcMe effected a sepn. into the *d*- and *l*-acids, the former being the less sol. The *d*-acid m. 211–2°,  $[\alpha]_D^{19} 57.7^\circ$  (0.48% in EtOH);  $[\alpha]_D^{19} 59.7^\circ$  (2.9% in EtOH);  $[\alpha]_D^{17} 74.7^\circ$  (5% in CHCl<sub>3</sub>). Shorter methods of isolation of the *d*-acid are also given. *Ozonide*, powder, m. 90° (decompn.). *Me ester*, b.<sub>0.05</sub> 149–50°,  $d_4^{19} 1.030$ ,  $n_D^{19} 1.52-08$ ; *Et ester*, b.<sub>0.2</sub> 169–70°,  $d_4^{14} 1.013$ ,  $n_D^{14} 1.5151$ . The value for *M<sub>p</sub>* agrees with the calcd. for 2 double bonds. Dihydro-*d*-pimaric acid, m. 239–40°,  $[\alpha]_D 14.5^\circ$  (0.5% in EtOH), rhomboids, *a*: *b*: *c* = 0.681: 1: 1.892, *c*(001), *m*(110), *q*(011), *a*(100), *c*: *q*, 62° 02', *a*: *m* 34° 16'. Heated with S for 15 hrs. (180–250°), a *hydrocarbon*, C<sub>16</sub>H<sub>14</sub>, m. 86°, results. *Picrate*, yellow, m. 131–2°; *stypnate*, yellow, m. 159°. Oxidation with CrO<sub>3</sub> in AcOH gave a *quinone*, C<sub>16</sub>H<sub>2</sub>O<sub>2</sub>, red, m. 166°, which with *o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> yields a *quinoxaline*, m. 194°. **XII. Fichtelite and the stereochemistry of hydrogenated phenanthrene derivatives.** L. RUZICKA, Fr. BALAS and H. SCHINZ. *Ibid* 692–7.—Although Bamberger and Strasser (*Ber.* 22, 3361) observed no reaction between fichtelite and S, it is now shown that from 30 g. and 25.7 g. S about 4 g. retene may be obtained. This definitely relates fichtelite (a product from peat) with retene and abietic acid, which may be an intermediate product in the formation of peat from the resin acids of the abietic acid group. Fichtelite has  $d_4^{20} 0.9185$ ,  $d_4^{22} 0.9380$ ,  $n_D^{19} 1.4942$ ,  $n_D^{20} 1.5052$ . The stereochemistry of hydrogenated phenanthrene derivs. is discussed.

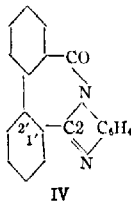
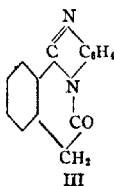
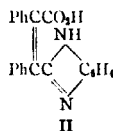
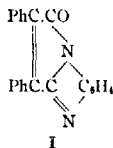
C. J. WESR

**Some fluoro derivatives of diphenyl.** THÉO VAN HOVE. *Bull. sci. acad. roy. Belg.* (v) 8, 505–30(1922); *Bull. soc. chim. Belg.* 32, 52–70(1923).—Ph<sub>2</sub> (500 g.) is nitrated in the cold with AcOH contg. 2 mols. of HNO<sub>3</sub> (d. 1.5). After a time, most of the 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Ph seps. and from the mother liquor, by pptn. with water, etc., and distn. under diminished pressure, is obtained, 2-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Ph (195 g.) b.<sub>0</sub> 200–5°, together with more 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Ph (350 g. in all). In the reduction of 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Ph with Sn and HCl, the sparingly sol. chlorostannate is best sepd. by filtration. 4-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Ph b.<sub>0</sub> 210–12°. 2-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Ph forms a sol. chlorostannate, and b.<sub>0</sub> at 189–91°. *4-Fluorodiphenyl*, obtained by diazotizing 4-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Ph in HF, and subsequently heating at 60°, m. 74.2°, b. 253°, and is volatile in steam. *2-Fluorodiphenyl*, obtained similarly, m. 73.5°, b. 243°, is also volatile in steam. The nitration of 4-FC<sub>6</sub>H<sub>4</sub>Ph in AcOH with HNO<sub>3</sub> (d. 1.5), gave 3 products: (a) *4-fluoro-4'-nitrodiphenyl*, m. 123°, giving *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H on oxidation; (b) an approx. equal wt. of *4-fluoro-2'-nitrodiphenyl*, m. 59–60°, giving, on oxidation, *p*-FC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H and (c) a very small quantity of *4-fluoro-2-nitrodiphenyl*, m. 53–4°, giving, on oxidation, *4-fluoro-2-nitrobenzoic acid*, m. 130°. In the first expt., but never subsequently, H. obtained pale yellow prisms, m. 43–43.5°, which, on keeping became opaque, and then m. 58°. This is apparently a case of dimorphism. *4-Fluoro-4'-aminodiphenyl*, obtained by the reduction of the corresponding NO<sub>2</sub> compd., m. 120°; *HCl salt*, sparingly sol. leaflets; *sulphate* and *oxalate*, very sparingly sol. leaflets; *Ac deriv.*, m. 205–5.5°. *4-Fluoro-2-aminodiphenyl*, m. 42–2.5°, b.<sub>0</sub> 186–7°, forms a *HCl salt*, m. about 210°, and a *sulfate*, which are much more sol. than the corresponding

salts of the 4'-deriv. The amine, on oxidation, gives  $p\text{-FC}_6\text{H}_4\text{CO}_2\text{H}$  and yields an *Ac deriv.*, m.  $120^\circ$ .  $4,2\text{-F}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{Ph}$ , on reduction, gives an amine, the *Ac deriv.* of which melts at  $98^\circ$ .  $2\text{-FC}_6\text{H}_4\text{Ph}$  gives rise to 3 isomeric  $\text{NO}_2$  derivs.: (a) a small quantity of needles, m.  $81^\circ$ , probably *2-fluoro-4-nitrodiphenyl*, since the *Ac deriv.*, m.  $155^\circ$ , of the amine obtained by reduction gives, on oxidation  $\text{BzOH}$ ; (b) *2-fluoro-4'-nitrodiphenyl*, yellow needles, m.  $74.5^\circ$ , giving on oxidation,  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$ , and (c) *2-fluoro-2'-nitrodiphenyl*, prisms, m.  $71.5^\circ$ , giving  $o\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$  on oxidation. *2-Fluoro-2'-aminodiphenyl*, m.  $91^\circ$ , gives a very sol. *HCl salt*, m. about  $205^\circ$ , a sol. sulfate, and an *Ac deriv.*, m.  $102^\circ$ . *2-Fluoro-4'-aminodiphenyl*, m.  $36^\circ$ , b<sub>m</sub>  $199\text{--}201^\circ$ , gives a sparingly sol. *HCl salt*, m. above  $250^\circ$ , a sparingly sol. sulfate, and an *Ac deriv.*, m.  $147\text{--}8^\circ$ . In the nitration of  $\text{Ph}_2$ , small quantities of a yellow, cryst. solid, m.  $202^\circ$ , probably *3,5,4'-trinitro-4-hydroxydiphenyl*, are formed.  $4\text{-FC}_6\text{H}_4\text{Ph}$ , similarly, gives rise to a small quantity of a solid,  $\text{C}_{16}\text{H}_9\text{O}_2\text{N}_2\text{F}(?)$ , probably a *fluorodinitrohydroxydiphenyl*.

J. C. S.

**Action of *o*-phenylenediamine upon the anhydrides of diphenylmaleic, homophthalic and diphenic acids.** A. BISTRZYCKI AND KARL FASSLER. *Helvetica Chim. Acta* 6, 519–35 (1923).—Diphenylmaleic anhydride and  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  in boiling  $\text{EtOH}$  give an 85–90% yield of *N*-[2'-aminophenyl]diphenylmaleic imide (diphenylmaleic-2'-aminoanil), orange-yellow, decomp.  $207\text{--}8^\circ$ . In spite of the free  $\text{NH}_2$  group, it is insol. in  $\text{HCl}$ . *Ac deriv.*, yellow, m.  $221^\circ$ . Heated above its m. p., the imide loses  $\text{H}_2\text{O}$ , forming 85% of [ $\alpha,\beta$ -diphenylacrylene]-2,1-benzimidazole (I), brown, m.  $186^\circ$ . The concd.  $\text{H}_2\text{SO}_4$  soln. is brownish red with a violet tinge. I also results by heating the components but in very poor yields. I, heated with  $\text{KOH}$  in  $\text{EtOH}$  and then acidified with  $\text{AcOH}$ , yields  $\beta$ -[benzimidazolyl-2']- $\alpha,\beta$ -diphenylacrylic acid (II), contains 1  $\text{H}_2\text{O}$ , gradually turns orange on heating and m.  $186^\circ$  (decompn.). After standing several days in abs.  $\text{EtOH}$ , it contains 1 mol.  $\text{EtOH}$ . *Et ester*, short needles, which yield I on heating. *Anilide*, m.  $278^\circ$  (decompn.). The condensation of  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  and homophthalic anhydride in boiling  $\text{EtOH}$  yields *2*-[carboxymethyl]-benz-[2'-aminoanilide],  $o\text{-HO}_2\text{CCCH}_2\text{C}_6\text{H}_4\text{CONHC}_6\text{H}_4\text{NH}_2(?)$ , turns yellow at  $150^\circ$  and then gradually m. *Ag salt*, sensitive to light. *o*-Phenylenecetyl-2,1-benzimidazole (III), yellow, m.  $345^\circ$  (decompn.), results upon heating the base at  $200^\circ$  for 10 min. It is not affected by  $\text{MeONa}$  in  $\text{MeOH}$ , concd.  $\text{NH}_4\text{OH}$  at  $100$  or  $200^\circ$ ,  $\text{PhNH}_2$  at  $190^\circ$  or boiling  $\text{PhNH}_2$ . Diphenic anhydride and  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  give a 71% yield of diphen-2'-aminoanilide-carboxylic acid,  $o\text{-HO}_2\text{CCCH}_2\text{C}_6\text{H}_4\text{CONHC}_6\text{H}_4\text{NH}_2$ , starts to decomp.  $123^\circ$ . From  $\text{EtOH}$  it seps. with 1 mol. of  $\text{EtOH}$  of crystals. Heated at  $150^\circ$ ,  $\text{H}_2\text{O}$  is evolved and a 70% yield of 2',1-[*o*-benzoylene]-2-phenylbenzimidazole (IV), m.  $177\text{--}8^\circ$  results, also



formed in about the same yield by heating the components at  $150^\circ$ . Unlike the 6-membered ring of III, this compd. yields 2'-[benzimidazolyl-2']-diphenyl-2-carboxylic acid, m.  $206\text{--}9^\circ$ . *Ag salt*. *Et ester*, m.  $143^\circ$  (decompn.). *Amide*, decomp.  $227^\circ$ . *Anilide*, decomp.  $248^\circ$ . *N*- $\beta$ -Phenylylhydrazide, decomp.  $157^\circ$ . \*A by-product in the production of IV is *N*-[2'-acetaminophenyl]diphenimide, decomp.  $233^\circ$ , which also results by heating the anilide with  $\text{AcCl}$ . It is probably  $(\text{C}_6\text{H}_5\text{CO})_2\text{NHC}_6\text{H}_4\text{NHAc}$ .

C. J. West



**The dibenzoylxylenes and the dinaphthanthracene diquinones.** HENRI DE DERSBACH. *Helvetica Chim. Acta* 6, 539-48 (1923).—2,5-Dicyano-1,4-dimethylbenzene (I), obtained by treating 1,4,2,5-C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>Br<sub>2</sub> with CuCN in C<sub>6</sub>H<sub>6</sub>N in an autoclave, m. 209.5-10°; boiled with 70% H<sub>2</sub>SO<sub>4</sub> it yields quant. β-cumidinic acid (II). II with PCl<sub>5</sub> gives the acid chloride, m. 116°. 4,6-Dicyano-1,3-dimethylbenzene (III) from 1,3,4,6-C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>Br<sub>2</sub>, m. 144-5°. III gives α-cumidinic acid (IV) with boiling 70% H<sub>2</sub>SO<sub>4</sub>. 4,6-Dibenzoyl-1,3-dimethylbenzene (V) from IV with PCl<sub>5</sub> and AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub>, m. 104°. In this prepn. the part that is sol. in alc. consists of a mixt. of IV with a new acid, 2,4-dimethyl-5-benzoylbenzoic acid, m. 149-50°. 1,3-Dimethyl-4,6-[2',5',2'',5''-tetrachlorodibenzoyl]benzene (VI), from the chloride of IV heated with p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> and AlCl<sub>3</sub>, m. 133-4°. The alk. ext. from this reaction gave 2,4-dimethyl-5-[2',5'-dichlorodibenzoyl]benzoic acid, m. 180°. 1,3-Dimethyl-4,6-[2',2''-dihydroxy-5',5''-dimethoxydibenzoyl]benzene (VII), m. 139-40°, is obtained by heating the chloride of IV with p-C<sub>6</sub>H<sub>4</sub>(OMe)<sub>2</sub> and AlCl<sub>3</sub>. During the steam distn. the sapon. of the two HO groups nearest the ketone group takes place. 2,5-Dibenzoyl-1,4-dimethylbenzene, from the chloride of II with C<sub>6</sub>H<sub>6</sub> and AlCl<sub>3</sub>, m. 160-1°. The alk. ext. from this prepn. gave 4-benzoyl-2,5-dimethylbenzoic acid, m. 151-2°. 1,4-Dimethyl-2,5-[2',5',2'',5''-tetrachlorodibenzoyl]benzene, from the chloride of II with p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> and AlCl<sub>3</sub>, m. 182°. The alk. ext. from this prepn. gave 4-[2',5'-dichlorodibenzoyl]-2,5-dimethylbenzoic acid, m. 193°. 2,5-[4',4''-Dimethyldibenzoyl]-1,4-dimethylbenzene, from the chloride of II with PhMe and AlCl<sub>3</sub>, m. 162°. 2,5-[4',4''-Dimethoxydibenzoyl]-1,4-dimethylbenzene, from the chloride of II with p-HOC<sub>6</sub>H<sub>4</sub>OMe and AlCl<sub>3</sub>, m. 177°. 4,6-[2',5',2'',5''-Tetrachlorodibenzoyl]benzene-1,3-dicarboxylic acid (VIII), from VI heated with HNO<sub>3</sub> in a sealed tube, m. 264-6° (decompn.). The di-Me ether of VIII, obtained by passing HCl through VIII in boiling MeOH, m. 178°. 1,4,8,11-Tetrachloro-5,7,12,14-dinaphthanthracene diquinone, from VIII heated in H<sub>2</sub>SO<sub>4</sub> decomp. without melting 340°. The NaHSO<sub>3</sub> salt is violet-blue. Other examples of this new synthesis will be discussed later. R. C. R.

**Action of organomagnesium compounds upon hydroxynitriles. I. Method for the preparation of substituted benzoin.** Y. ASAHINA AND M. TERASAKA. *J. Pharm. Soc. Japan* 494, 219-28 (1923).—20 cc. concd. HCl are added in drops while shaking an ice-cold mixt. of 20 g. freshly distd. BzH and 13 g. KCN. After 1 hr. the product is dissolved in C<sub>6</sub>H<sub>6</sub> and dehydrated with Na<sub>2</sub>SO<sub>4</sub>. The PhMgBr from 235 g. PhBr, 3.6 g. Mg and 75 cc. abs. Et<sub>2</sub>O is added in drops to the above cyanohydrin in C<sub>6</sub>H<sub>6</sub> and the mixt. is heated 5 hrs. on the water bath. The Mg compd. is decompd. by ice and dil. H<sub>2</sub>SO<sub>4</sub>. From the C<sub>6</sub>H<sub>6</sub>-Et<sub>2</sub>O layers, by steam distn., biphenol is distd., and the resinous residue on recrystn. from MeOH gives crystals m. 137° (0.7 g. yield). From the aq. acid layer, there slowly sep. on long standing, crystals, which also m. 137°. The total yield is 32.7% of theoretical. Their compn. and properties are the same as those of benzoin prepd. by other methods. By a similar method, from furfural cyanohydrin and PhMgBr A. and T. obtained isobenzofuroin, C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>, m. 119°, which on oxidation with Fehling soln. gives benzofuril, m. 41°. From p-MeOC<sub>6</sub>H<sub>4</sub>CH(OH)CN, m. 62°, and PhMgBr, p-methoxybenzoin, m. 89°, is obtained (40.5% yield). o-HOC<sub>6</sub>H<sub>4</sub>CH(OH)CN and PhMgBr give o-hydroxybenzoin, m. 148°. o-MeOC<sub>6</sub>H<sub>4</sub>CH(OH)CN and PhMgBr give o-methoxybenzoin, m. 58°, which on oxidation with Fehling soln. at room temp. gives quant. o-methoxybenzil, m. 71.5°. From the benzil, by treatment with alkali (Liebig), is obtained o-methoxybenzoic acid, m. 100-1°. From o-MeOC<sub>6</sub>H<sub>4</sub>CH(OH)CN and p-MeOC<sub>6</sub>H<sub>4</sub>MgBr, o,p'-dimethoxybenzoin, m. 92-3°, is prepd. and with Fehling soln. gives o,p'-dimethoxybenzil, m. 105°. From this benzil on alk. treatment, o,p'-dimethoxybenzoic acid, m. 161-2°, is obtained. S. T.

**Semipinacolic transpositions. I. Dehydration of aryldialkylglycols by heat and by acids.** M. TIFFENEAU AND J. LEVY. *Bull. soc. chim.* 33, 735-59 (1923).—Aryldialkylglycols may dehydrate and undergo subsequent transposition in two ways, by the elimination of the tertiary OH followed by a semihydrobenzoic transposition, which is the normal reaction for these glycols, or by the elimination of the secondary OH followed by a semipinacolic transposition (C. A. 15, 3477). The tertiary OH increases in stability as the alkyl radicals become heavier. The phenylmethyl-ethyl- and phenyldiethylglycols have a max. hypnotic effect on mice and dogs, but the higher homologs give the max. effect with fish. Phenyldiethylglycol (I) b<sub>10</sub> 163-5°, m. 89°, was prepd. from EtMgI and PhCH(OH)CO<sub>2</sub>Et. 3-Phenyl-4-hexanone (II) obtained by the action of cold H<sub>2</sub>SO<sub>4</sub> on I, and purified through the semicarbazone (m. 139-40°), b<sub>11</sub> 114-6°, d<sub>20</sub> 0.935, d<sub>4</sub> 0.978; oxime, m. 57-8°. II was also prepd. directly by the dehydration of 3-phenyl-3,4-hexanediol with cold concd. H<sub>2</sub>SO<sub>4</sub>. 1-Phenyl-2-ethyl-1-butanone was prepd. for comparison. Diethylstyrene oxide (III), b<sub>12</sub> 120-8°, b. 232-6°,

was obtained by the action of  $P_2O_5$  on **I**, and by heating **I** with  $(CO_2H)_2$ . With cold concd.  $H_2SO_4$  **III** undergoes a semipinacolic transposition giving **II**. Dil.  $H_2SO_4$  or 50%  $(CO_2H)_2$  boiled with **I** gives *phenyldiethylacetaldehyde* (**IV**),  $b_{20}$  110–21°,  $d_4$  0.996 (semicarbazone, m. 181°), and **III** by the semihydrobenzoic transposition. **I** distilled alone yields **III** and **IV**. *Phenyldipropylglycol* (**V**), from  $PrMgI$  and  $PhCH(OH)CO_2Et$ , m. 100–1°,  $b_{20}$  175–80°,  $b$  290–300°. *4-Phenyl-5-octanone* (**VI**),  $b_{20}$  140–2°,  $d_4$  0.952 (semicarbazone, m. 107–8°), was obtained by the action of cold concd.  $H_2SO_4$  on **V**. **VI** was also obtained by the dehydration with concd.  $H_2SO_4$  of *4-phenyl-4,5-octanediol* (**VII**),  $b_{18}$  178–9°, m. 59–60°. **VII** was prepd. from  $PhMgI$  and butyrol.  $H_2SO_4$  (1:2) refluxed with **V** gave *phenyldipropylacetaldehyde*, semicarbazone, m. 160–1°. By the semihydrobenzoic transposition, a substance believed to be *dipropylacetophenone* was obtained. *Phenyldibutylglycol* (**VIII**),  $b_{20}$  220–30°,  $b$  330–40°, was prepd. from  $BuMgI$  and  $PhCH(OH)CO_2Et$ . With cold concd.  $H_2SO_4$  it gave *6-phenyl-5-decanone*,  $b$  285–7°,  $d_4$  0.934; semicarbazone, m. 100–1°; oxime, m. 55–6°.  $H_2SO_4$  (1:1) refluxed with **VIII** gave *dibutylacetophenone* (**IX**),  $b_{20}$  170–6°,  $d_4$  0.936. **IX** was also prepd. by the action of  $Bu_2CHCOCl$  on  $C_6H_5$  in the presence of  $AlCl_3$ . *Phenyldibenzylglycol* (**X**), m. 110–11°, was prepd. from  $C_6H_5MgCl$  and  $PhCH(OH)CO_2Et$ . With cold concd.  $H_2SO_4$  it gave *1,3,4-triphenyl-2-butanone*. Dil.  $H_2SO_4$  gives the same product since the benzyl groups are heavy enough to stabilize the tertiary OH, thus preventing the semihydrobenzoic transposition. No dehydration is obtained by distg. **X**. *Anisyl-diethylglycol*, m. 78–9°, prepd. from  $EtMgBr$  and  $MeOC_6H_4CH(OH)CO_2Et$ . Refluxed with  $H_2SO_4$  it gave *anisyl-diethylacetaldehyde*,  $b_{20}$  165–7°; semicarbazone, m. 131–2°. The same product was obtained by direct distn. **II**. **Migratory aptitudes of acyclic radicals in pinacolic and semipinacolic transpositions.** *Ibid* 759–79.—The radicals  $Et$  and  $PhCH_2$  were successively opposed to  $Me$  in structurally identical positions and were found to migrate in preference to  $Me$  in both pinacolic and semipinacolic transpositions. Methyl-ethyl- and methylbenzylstyrene with  $HIO$  gave iodohydrins, which by the action of  $KOH$  or  $AgNO_3$  lost  $HI$  and gave ketonic products of transposition. The other iodohydrins of this series, however, lose  $HIO$  and regenerate the styrene. To study other radicals, glycols of the form  $PhCH(OH)C(OH)RR'$  were prepd. from  $R'MgX$  and ketone aces. of the form  $PhCH(OH)COR$ . *Phenylmethylstyrylglycol* (**I**), m. 85°, was prepd. from  $EtMgBr$  and  $PhCH(OH)COMe$ . *3-Phenyl-2-pentanone* (**II**), (semicarbazone, m. 189°) was obtained by the action of cold concd.  $H_2SO_4$  on **I** through the migration of the  $Et$ . **II** was also prepd. directly from  $PhCH_2COMe$ ,  $EtBr$ , and  $EtONa$ . *2-Phenyl-3-pentanone* (semicarbazone, m. 136°) was obtained directly from hydratropic aldehyde and  $EtMgBr$ , giving *2-phenyl-3-pentanol*,  $b_{20}$  134–7°, which was then oxidized to the pentanone by  $Cr_2O_3$ . *1-Phenyl-2-methyl-3-butanol* was obtained from  $EtMgBr$  and  $PhCH_2COMe$  and then was dehydrated by concd.  $H_2SO_4$  in  $Ac_2O$ , giving *methyl-ethylstyrene* (**III**),  $b_{20}$  98–100°,  $b$  199–200°,  $d_4$  0.924 (63% yield). **III** in  $Et_2O$  with  $HgO$  and **I** gave *phenylmethylglycol iodohydrin* (**IV**), thick yellow product, turning brown in the air. **II** was obtained by the action of  $AgNO_3$  on **IV** and identified by its semicarbazone, m. 189°. **IV** with  $KOH$  gave **II**, also methyl-ethylstyrene oxide and regenerated some **III**. *Methyl-ethylstyrene oxide*,  $b$  205–7°,  $d_4$  0.933, treated with cold concd.  $H_2SO_4$  gave **II**. *1,1-Diphenyl-2-benzyl-1,2-propanediol* (**V**), m. 81–2°, was prepd. in 57% yield from  $PhMgBr$  and  $PhCH_2CMe(OH)CO_2Et$ . Cold concd.  $H_2SO_4$  reacts with **V**, the  $PhCH_2$  migrating to form *1,2,2-triphenylbutanone* (**VI**), m. 66°. **VI** was obtained directly by benzylating *1,1-diphenyl-2-propanone*, which had been obtained by the dehydration of *1,2-diphenylpropanediol*. *Phenylbenzylmethylglycol iodohydrin* (**VII**) was prepd. by the action of  $HIO$  on *benzylmethylstyrene*,  $b_{20}$  180–3°,  $d_4$  1.039, which had first been prepd. by dehydrating *1,3-diphenyl-2-methylpropanol*,  $b_{20}$  194–9°. *3,4-Diphenyl-2-butanone* (**VIII**) (semicarbazone, m. 143–4°; oxime, m. 134–5°) was obtained by the action of  $AgNO_3$  on **VII**, the  $PhCH_2$  migrating in preference to the  $Me$ . **VIII** was also obtained by the action of  $KOH$  on **VII**. **VIII** was prepared directly by benzylating  $PhCH_2COMe$ .

A. C. PURDY

**Strychnos alkaloids. XXXVIII. Transformations of the four isomeric brucine-sulfonic acids.** HERMANN LEUCHS and HEINZ ZANDER. *Ber.* 56B, 502–9(1923); cf. C. A. 17, 2714.—The brucinesulfonic acid **I**, treated with  $NHNO_3$  and warmed for 15 min. on the  $H_2O$ -bath, gives the orange-red *nitroquinonehydrate*,  $C_{20}H_{21}O_4N_2S$  (**I**), which loses at 130° in vacuum 1.1 to 1.8 mols.  $H_2O$ ; semicarbazone, citron-yellow. Reduction of **I** in  $HCl$  with  $Sn$  gives the *aminohydroquinol hydrochloride*, thick prisms, which are oxidized in alk. soln. by the  $O$  of the air. Reduction by  $SO_2$  (heating in a sealed tube at 100° for 6 hrs.) gives the dark violet *nitrohydroquinol hydrate*, easily oxidized to **I**. The red-violet *di-Et ester* is slowly oxidized in alk. soln to **I**. *Triacetate*,

yellow, is sapond. by alkali. Brucinesulfonic acid III yields a *nitroquinone hydrate*, orange plates contg. 3 H<sub>2</sub>O. The *hydroquinol hydrate* is dark violet. Brucinesulfonic acid IV, treated with 5 N HNO<sub>3</sub>, gives a *quinone nitrile*, C<sub>21</sub>H<sub>10</sub>O<sub>7</sub>N<sub>2</sub>S.HNO<sub>3</sub>, red plates contg. 5 H<sub>2</sub>O. The *nitroquinone hydrate*, obtained by warming the reaction product at 100° for 10 min., orange prisms with 1 H<sub>2</sub>O of crystn. The *hydroquinol hydrate* forms light reddish violet needles or dark reddish violet prisms, contg. 3 H<sub>2</sub>O. The reaction of satd. Br-H<sub>2</sub>O upon nitroquinone hydrate I (from acid I) gives the *compd.* C<sub>21</sub>H<sub>12</sub>O<sub>11</sub>N<sub>2</sub>Br<sub>2</sub>S.2H<sub>2</sub>O, yellowish, decomp. in hot H<sub>2</sub>O, liberates I from KI and, when crystd. from H<sub>2</sub>SO<sub>4</sub>, appears to change to the *compd.* C<sub>21</sub>H<sub>12</sub>O<sub>11</sub>N<sub>2</sub>S (II), yellow plates contg. 11% H<sub>2</sub>O. Reduction of II by Sn and HCl gives a *compd.* C<sub>21</sub>H<sub>12</sub>O<sub>7</sub>N<sub>2</sub>S.HCl.3H<sub>2</sub>O; the aq. soln. gives a wine-red color with FeCl<sub>3</sub>. Br reacts with II to give a new *compd.*, C<sub>21</sub>H<sub>12</sub>O<sub>7</sub>N<sub>2</sub>SBr<sub>2</sub>, which liberates I from KI; heating with H<sub>2</sub>O causes the evolution of O<sub>2</sub>NCBr<sub>4</sub> and the formation of the *compd.* C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>S, crystals contg. 3H<sub>2</sub>O.

C. J. WEST

**Total hydrogenation of naphthalic (naphthalene-1,8-dicarboxylic) acid.** J. CA-SARES AND J. RANEDO. *Anales soc. españ. fis. quim.* 20, 519-26(1922).—1,8-C<sub>10</sub>H<sub>6</sub>(CO<sub>2</sub>H)<sub>2</sub> was hydrogenated to the tetrahydro and decahydro acids by the action of H in the presence of Pt. Specially purified reagents were used, and repeated activations were necessary. The decahydronaphthalene-1,8-dicarboxylic acid thus obtained has no definite m. p., and is probably a mixt. of *cis*- and *trans*-isomerides. Hydrogenation was effected more easily and without activation by use of the Me and Et esters of naphthalic acid. *Me tetrahydronaphthalene-1,8-dicarboxylate* thus obtained from Me naphthalate forms crystals, m. 74°. *Et tetrahydronaphthalene-1,8-dicarboxylate*, m. 52°, and bp 193°. *Me decahydronaphthalene-1,8-dicarboxylate*, m. 103-5°. J. C. S.

**Amino alcohols of tetralin [tetrahydronaphthalene].** A. GONZÁLEZ AND M. CAMPOV. *Anales soc. españ. fis. quim.* 20, 534-8(1922).—By the action of HBrO on 1,4-dihydronaphthalene, is obtained 3-bromo-2-hydroxytetrahydronaphthalene, m. 107°. By acting on it with anhyd. NHMe<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> in a sealed tube at 120° is obtained 3-dimethylamino-2-hydroxytetrahydronaphthalene, b<sub>14</sub> 165-70°. 2-Dimethylamino-1-hydroxytetrahydronaphthalene, b<sub>11</sub> 157-8°. The following HCl salts were also prepd: 2-benzoyl-3-dimethylaminotetrahydronaphthalene, m. 228°; 2-valeryl-3-dimethylaminotetrahydronaphthalene, m. 173°; 2-cinnamoyl-3-dimethylaminotetrahydronaphthalene, m. 178°; 2-pyromucyl-3-dimethylaminotetrahydronaphthalene; 1-benzoyl-2-dimethylaminotetrahydronaphthalene, m. 176°; 1-valeryl-2-dimethylaminotetrahydronaphthalene, m. 165°; 1-cinnamoyl-2-dimethylaminotetrahydronaphthalene, m. 176.5°; 1-pyromucyl-2-dimethylaminotetrahydronaphthalene, m. 172°. HCl salts of the 1,2-series are more sol. and have a lower m. p. than those of the 2,3-series. J. C. S.

**Several addition compounds of digitonin.** A. WINDAUS AND R. WEINHOLD. *Z. physiol. Chem.* 126, 299-307(1923).—Digitonin addn. *compds.* with α-naphthol, β-naphthol, p-bromonaphthol, thiophenol, carvomenthol, l-α-terpineol, d-α-terpineol, acetetahydro-β-naphthol, α-phenylethyl alc., and sec-octyl alc. were prepd. by mixing solns. of digitonin and the appropriate *compd.* All of them are fairly insol. and the amt. of H<sub>2</sub>O of crystn. in each is somewhat variable. By extn. with Et<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>, or xylene resoluion into the constituent *compds.* takes place with different degrees of ease. *Compds.* which are not alcs., phenols or thiophenols do not react with digitonin.

R. L. STEHLE

**A method for separating a racemic alcohol into its optically active components.** A. WINDAUS, F. KLÄNHARDT AND R. WEINHOLD. *Z. physiol. Chem.* 126, 308-12(1923); cf. preceding abstr.—dl-α-Terpineol and dl-ac-tetrahydro-β-naphthol were sep'd. into their active components by pptn. with digitonin. Attempts to sep. i-carvomenthol and MeCHPhOH were unsuccessful. R. L. STEHLE

**The constitution of sinigrin, the glucoside of mustard oil.** FRITZ WREDE, EMIL BANK AND OTTO BRAUSS. *Z. physiol. Chem.* 126, 210-8(1923).—Thioglucoase from sinigrin (I) was compared with the synthetic *compd.* (II) in a no. of ways. The Ag salt and the penta-Ac deriv. of I neither cryst. nor melt sharply; the optical rotation of I is — while that of II is +. For the acetates of I and II [α]<sub>D</sub> —50° and [α]<sub>D</sub> 1.5, resp. If to sinigrin in abs. MeOH twice the vol. of EtOH is added and the soln. boiled a white *cryst.* mass m. 179° ppts. This behavior is believed to indicate that sinigrin is not C<sub>10</sub>H<sub>14</sub>NS<sub>2</sub>KO<sub>10</sub> but C<sub>10</sub>H<sub>14</sub>NS<sub>2</sub>KO<sub>8</sub>H<sub>2</sub>O. Its decompn. by myrosin is, therefore, a hydrolytic reaction. R. L. STEHLE

**Rupture of the furan nucleus.** A. FUJITA. *J. Pharm. Soc. Japan* 493, 148-56(1923).—Reactions involved in 3 different methods of rupture of the furan nucleus (Stenhouse, Baeyer and Markwald's) are considered first in detail. In order to see the extent of the applicability of B.'s method, Br and Ag<sub>2</sub>O treatments were tried on

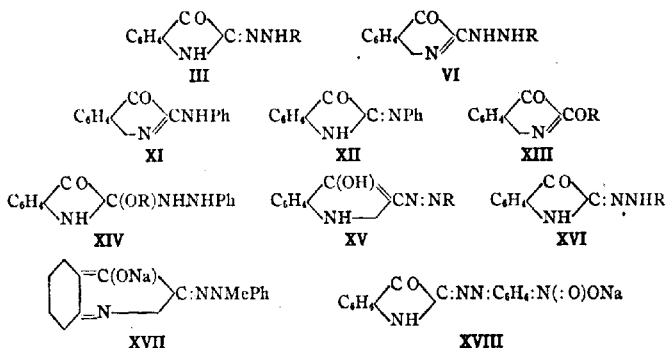
furylacetone, furyllevalinic acid,  $\delta$ -furylbutaneaminobenzaldehyde and furylvalerolactone. To 14 g. furylacetone,  $b_{11}$  88°, in 50 cc. dil. alc. 16 g. of Br is added in drops. An immediate decolorization occurs. The transparent liquid becomes deep red with alkali and has a strong reducing action—evidence that a ketoaldehyde is present. 8.5 g. of freshly prepd.  $\text{Ag}_2\text{O}$  is then added and heated for 2 hrs. at 80–5°. After treatment with  $\text{HCl}$ ,  $\text{Et}_2\text{O}$ , and  $\text{Na}_2\text{CO}_3$ , acid and  $\text{Et}_2\text{O}$  in the usual manner are formed about 2.5 g. of brownish prisms,  $m.$  116°, of  $\text{MeCOCH}_2\text{CH}_2\text{COCH}:\text{CHCO}_2\text{H}$  (I). When I was reduced with Pt black and  $\text{H}_2$ , F. obtained  $\gamma,\delta$ -diketooctane acid,  $m.$  76°. This rupture of furylacetone, which was not possible by M.'s method (Harries and Kaiser, *Ber.* 32, 1320), can be effected by B.'s method. The successful rupture of furyllevalinic acid to anemonic acid has already been reported. A supplementary note describes the prepn. from furylpropionic acid by B.'s method of the acid  $\text{HO}_2\text{CCH}:\text{CHCOCH}_2\text{CH}_2\text{CO}_2\text{H}$ , which  $m.$  185°, not 180°, as B. states.

**Derivatives of indole.** S. KURODA. *J. Pharm. Soc. Japan* 403, 131–2 (1923).—By using Fischer's method of synthesis of indole derivs. with phenylhydrazones and  $\text{ZnCl}_2$  K. prepd. various indole derivs. (1) From benzylacetone. The formation of the hydrazone,  $m.$  50°, is smooth.  $\alpha$ -Methyl- $\beta$ -benzylindole, prepd. by  $\text{ZnCl}_2$  from the hydrazone,  $m.$  116°, gives a positive *pine splinter test* (designated as S. test). (2) From  $\text{BuCOMe}$  was obtained  $\alpha$ -methyl- $\beta$ -propylindole, oil,  $b_{10}$  195°, gives a positive S. test. (3) From iso- $\text{BuCOMe}$ ,  $\alpha$ -methyl- $\beta$ -isopropylindole,  $b_{16}$  173°. (4) From  $\text{C}_6\text{H}_5\text{COMe}$ ,  $\alpha$ -methyl- $\beta$ -octylindole,  $b_{18}$  230–5°. From the phenylmethylhydrazones were obtained the  $\beta$ -benzyl,  $\beta$ -propyl and  $\beta$ -octyl derivs.,  $b_{18}$  235°,  $b_{18}$  187° and  $b_{18}$  225–30°, resp., of  $N,\alpha$ -dimethylindole. With camphor phenylhydrazone 3 fractions were obtained: (a)  $\text{Et}_2\text{O}$ -sol.; (b) acid-sol.; and (c)  $\text{Et}_2\text{O}$ -insol. and acid-insol. oil. (a) is camphoride,  $b_{18}$  210–5°, and if left in petroleum ether, deposits,  $m.$  91°; (b) with alkali ppts. a compd.,  $\text{C}_{14}\text{H}_{22}\text{N}_2$ ,  $m.$  201°, which has the same compn. as the polycamphorphenylhydrazone reported by Cazeneuve, but properties are quite different. (c) Boiled with alkali produces a cryst. substance  $m.$  207° identical with (b). In this reaction, if the heating is slightly modified,  $\text{PhNH}_2$  is obtained instead of  $\text{C}_{14}\text{H}_{22}\text{N}_2$ . With menthone two products are formed (a) menthoneindole,  $\text{C}_{14}\text{H}_{22}\text{N}_2$ , insol. oil,  $b_{18}$  213°, which does not give the S. test; (b) a basic mixt. contg.  $\text{PhNH}_2$  and  $\text{C}_{14}\text{H}_{22}\text{N}_2$ ,  $b_{18}$  181°; the latter is probably menthoindoline, whose mono-Bz deriv.  $m.$  163°.

S. T.

**Azo compounds of indoxyl and  $\alpha$ -hydrazinoisatin.** O. DORNIER AND J. MARTINET. *Rev. gen. mat. color.* 28, 65–7, 84–5 (1923); cf. *C. A.* 14, 2623, 2919; 15, 2093, 3448, 4007.—Indoxyl (I) has a constitution and properties resembling those of  $\text{PhOH}$  and as such combines with diazo compds. Baeyer (*Ber.* 16, 2190 (1883)) coupled I with  $\text{PhN}_2\text{Ph}$  and the resulting compd. may also be formed by treating  $\text{PhNHNH}_2$  with  $\alpha$ -anilinoisatin (II); the compd. was considered to be isatin  $\alpha$ -phenylhydrazone (III). II exists in 2 forms, as the true  $\alpha$ -anilide (XI), stable in  $\text{CaH}_2$ , and the  $\alpha$ -anil form (XII). The compd. may be considered as  $\alpha$ -phenylhydrazinoisatin (VI) since the reaction is effected in  $\text{C}_6\text{H}_6$ . The same reaction is effected by replacing II by an  $O$ -alkylisatin of the formula XIII. These modes of synthesis do not fix the formula because in the last mentioned case are formed colorless compds. of the probable formula XIV. This compd. on loss of alc. gives the desired product. Hitherto it has been the choice of an azo indoxyl (XV), and an  $\alpha$ -phenylhydrazone (III), but an  $\alpha$ -phenylhydrazinoisatin (VI) is possible. III is incompatible with the strong red color of the compd. obtained. The chromophores  $=\text{C}:\text{O}$  and  $=\text{C}:\text{N}$  are of the same strength but a direct union of an auxochrome to a chromophore generally results in a diminution of color as in the case of phenylhydrazones, which possess the chromophore  $=\text{C}:\text{N}$  directly joined to  $\text{NHR}$ . Phenylhydrazones are less colored than the ketones from which they are derived. Comparison of red isatins with their yellow  $\beta$ -arylhydrazones is an instance. We would expect an easy reaction with  $\text{PhNHNH}_2$  but the osazone is prepd. only at a high temp. Supporting the phenylhydrazone formula mention has been made of the decarboxylation when  $\text{PhN}_2\text{Cl}$  reacts with indoxyl acid, but this acid is easily decarboxylated. The coloration of the condensation products of I with diazo compds. is explained equally well by XV and VI; the coloration approaches that of several  $\alpha$ -hydroxyazo compds., on the one hand and of II on the other. Benzeneazoidoxyl (VII) dissolves in alkali with a deepening of the color, following the rule for all hydroxy coloring matters.  $\text{CO}_2$  reppts. VII, a fact supporting XV. VI may result, when II is condensed with  $\text{NH}_2\text{NMePh}$  and in this case an azo compd. is evidently impossible. The resulting compd. has a striking analogy with II in that the alc. soln. turns malachite green with  $\text{KOH}$ . The structure may be XVII. It dissociates in  $\text{H}_2\text{O}$  giving a red color. Compds. related to III are the intensely colored alkali salts of  $o$ - and  $p$ -nitrobenzene-

azoindoxyl of the type **XVIII**. The alc. soln. dild. with  $H_2O$  turns from blue-green to red. On elevating the temp., it becomes blue and becomes red again on cooling. *Phenylmethylhydrazinoisatin* (**X**), m.  $190^\circ$ , was prepd. by refluxing for 1 hr. II in  $C_6H_6$  and adding  $MePhNNH_2$ . The soln. darkens slowly.  $BzPhNNH_2$  would not react under the same conditions.



**Pictet's synthesis of tetrahydroisoquinoline.** H. KONDO AND H. OCHIAI. *J. Pharm. Soc. Japan* **495**, 313-9(1923).—When 100 g. of methylal is added in drops to 100 g. of  $PhCH_2CH_2NH_2$  in 600 cc. concd. HCl on the water bath and heated for 10 hrs., a yellow sirupy residue is obtained on removal of HCl by distn. under diminished pressure. After treating the aq. soln. of this residue with alkali, the free base is shaken out by  $Et_2O$ . The ext. contains 2 fractions (I), b.  $70-120^\circ$  (mainly at  $84^\circ$ ), and (II), b.  $200-50^\circ$  (mainly at  $210^\circ$ ). I with  $Na_2SO_4$  gives a reddish brown oil (35 g.), having a cinnamon odor, and gives Liebermann's NO reaction. This with Sn and HCl gives  $PhCH_2CH_2Cl$ , a yellow oil, b.  $198-202^\circ$ . From the aq. portion, is obtained, tetrahydroisoquinoline-HCl, m.  $195-7^\circ$ . Thus most of I consists of phenylethylamine and a small amt. of tetrahydroisoquinoline. II gives white crystals and a brownish amorphous powder, the former being the HCl salt of diphenylethylammonomethane (which does not m.  $300^\circ$ ; the Pt.  $K_2Cr_2O_7$  and  $HgCl_2$  salts also do not m. at  $280^\circ$ ; Au salt m.  $118-20^\circ$ ). The free base m.  $150-1^\circ$ , and takes up  $CO_2$  easily. By Pictet's synthesis in a sealed tube at  $130-50^\circ$  for 4 hrs., K. and O. obtained a trace of tetrahydroisoquinoline, and a yellow amorphous base, which is  $Et_2O$ -insol.,  $CHCl_3$ -sol. The compn. of the latter is not yet detd. with certainty, but judging from the analysis of the impure compd., it may be a condensation product of 1 amine mol. with several mols. of  $CH_2O$ . The conclusion is that, Pictet's synthesis is not so simple as to support Wintersten and Trier's idea that natural isoquinoline (whose pyridine nucleus is always satd. with H), is formed by condensation of aldehyde and  $EtNH_2$  derivs., produced from protein (cf. Decker and Becker, *C. A.* **7**, 1512).

H. E. W.

S. T.

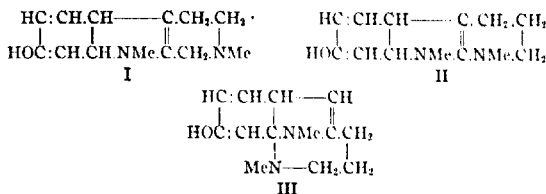
**Ability of alkaloids to form oxides. Oxygenase of the Bach-Chodat system.** OBDULIO FERNÁNDEZ AND ANTONIO PIZARRRO. *Anales soc. españ. fis. quim.* **20**, 589-94(1922); cf. Fernández, *C. A.* **16**, 1261.—The ability of a no. of alkaloids and other compds. contg. the group  $-CO.NH-$  to form oxides in the presence of  $H_2O_2$  is investigated. The conclusions drawn are indefinite.

J. C. S.

**Dimethiodides in the eserine series.** MAX POLONOVSKI AND MICHEL POLONOVSKI. *Compt. rend.* **176**, 1813-5(1923).—Eseroline, ethoxyeseroline and its *N*-Me deriv., when heated with an excess of MeI, yield a mixt. of mono- and dimethiodides. Eserine gave no di-deriv. The dihydro derivs. of the eserine series yielded stable methiodides almost quant. The latter were not attacked by dil., concd. or hot alkalis. Evidence is given to show (1) that eserine and eseroline in alc. undergo exhaustive methylation, (2) that the OH becomes OMe, (3) that a second Me is fixed on the basic N, (4) that the two other entering Me groups destroy the double bond, (5) that two MeI are fixed, one to each N. The dimethiodide, (1) of eserine and eseroline,  $C_{17}H_{25}Me_2(OH) \cdot NMe_2 \cdot NMe_2$ , m.  $235^\circ$ ; (2) of their dihydro derivs. m.  $205^\circ$ , while  $C_{17}H_{25}Me_2(OEt)OH \cdot NMe_2 \cdot NMe_2$ , m.  $207^\circ$ .

R. L. BROWN

**The constitution of eserine.** MAX POLONOVSKI AND MICHEL POLONOVSKI. *Compt. rend.* 176, 1896-8 (1923).—On the basis of their researches P. and P. set up these facts on which, together with other evidence, the tentative formulas below are proposed: (1) Eserine is a methylurethan of a base with phenolic properties, eseroline. (2) It possesses 2 tertiary N atoms, one basic, which are both tied to a Me. (3) The mol. contains 1 double bond easily hydrogenated. (4) Eserine and all its degradation products studied possess at least one asym. C atom.



The formulas of Salway (*C. A.* 7, 2217) and Strauss (*C. A.* 8, 497) are rejected.

R. L. BROWN

**Acetic acid.** J. E. HAGGENMACHER. U. S. 1,463,209, July 31. Successive batches formed from  $\text{Ca}(\text{OAc})_2$ , HCl and a soln. of HOAc are distd. under reduced pressure. The distillate is cut into a first coned. HOAc fraction and a later dil. HOAc fraction and the dil. HOAc fraction from each batch is used for the prepn. of the next succeeding batch.

**Concentrated acetic acid.** H. HOWARD. U. S. 1,463,212, July 31. A mixt. formed from  $\text{Ca}(\text{OAc})_2$ , HCl gas and  $\text{H}_2\text{O}$  is partially distd. by indirectly heating the mixt., a relatively concd. HOAc is collected during the distn. and the distn. of the HOAc content of the mixt. is completed by indirectly heating it and by blowing live steam through it to obtain a relatively dil. HOAc soln.

**Methyl acetate and other esters.** C. B. CARTER AND A. E. COXE. U. S. 1,459,971, June 26. MeCl is heated under pressure with NaOAc in the presence of dil. alc. or MeOAc to produce MeOAc. Various other esters may be similarly formed from halogenated hydrocarbon derivs., e. g., EtCl,  $\text{C}_3\text{H}_7\text{Cl}$ ,  $\text{C}_4\text{H}_9\text{Cl}$ , isobutyl chloride, MeI or MeBr, org. salts such as oxalates, formates, butyrates, benzoates or salicylates of Na or K, in the presence of solvents by the action of heat and pressure. E. g., Et butyrate may be formed from EtCl and Na butyrate, and Me salicylate from MeCl and Na salicylate.

**Benzoic acid and benzoates.** E. O. BARSTOW. U. S. 1,463,190, July 31.  $\text{PhCH}_2\text{Cl}$  is oxidized to BzOH by the action of bleaching powder in the presence of  $\text{H}_2\text{O}$  and excess lime, under pressure.

**Benzoic acid from dibenzyl.** G. O. CURME, JR. and H. B. HEYN. U. S. 1,463,255, July 31. Dibenzyl is oxidized by use of molecular O in the presence of an O-carrier such as  $\text{MnO}_2$  and NaOH at 150-500° to produce a benzoate; from this benzoic acid is prepd.

**2-Hydroxy-1-phenylnaphthylamine.** A. WAHL and R. LANTZ. U. S. 1,400,774, July 31. 2-Hydroxy-1-phenylnaphthylamine, white needle-form crystals, m. 153-4°, insol. in cold  $\text{H}_2\text{O}$  and slightly sol. in boiling  $\text{H}_2\text{O}$ , and sol. in caustic alkalis (from which solns. acids ppt. the original compd.), is prepd. by boiling together  $\alpha$ -chloro- $\beta$ -naphthol 1 and aniline 5 parts under a reflux condenser for 3-4 hrs., distg. off excess starting materials by steam, dissolving the residue with alkali, pptg. with acid and purifying by crystg. from  $\text{C}_6\text{H}_6$  and then from a mixt. of HOAc and  $\text{HCOOH}$ . 2-Hydroxy-1-*p*-tolyl-naphthylamine, white crystals, m. 137-8°, may be similarly obtained from  $\alpha$ -bromo- $\beta$ -naphthol and *p*-toluidine.

**Purifying anthraquinone.** F. W. TRACK. U. S. 1,461,745, July 17. Crude dry anthraquinone is purified by recrystg. from a phenol- $\text{H}_2\text{O}$  mixt. (approx. phenol monohydrate in compn.).

**Dihydroxyperylene.** PEREIRA, II. Brit. 191,363, Nov. 15, 1922. Dihydroxyperylene is obtained by heating dihydroxydinaphthyl with ring-closing condensing agents, such as  $\text{AlCl}_3$ . Basic substances, such as the oxides, hydroxides or carbonates of alkali and alk. earth metals, are preferably added to the mixt. Cf. 106,770 and 165,771 (*C. A.* 16, 721).

## 11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

**Biochemical action of polarized light.** E. C. BRYANT. *Chemistry & Industry* 42, 681 (1923).—Pieces of fish exposed to polarized light for 12–14 hrs. were highly putrefied whereas control pieces, unexposed to light, remained fresh. Apparently the prejudice in tropical climates against the use of fish or meat that has been exposed to moonlight has a sound basis as moonlight is largely polarized light which apparently hastens putrefactive changes.

F. A. CAJORI

**The potential acidity in colloidal complexes of living organisms and their activation by a few physical agents.** ALBERTO SCALA. *Ann. d' Ig.* 31, 743–55; *Chem. Zentr.* 1922, III, 883; cf. *C. A.* 15, 2644.—If finely divided plant and animal tissue is repeatedly washed with distd.  $H_2O$ , the first wash- $H_2O$  upon concn. gives an acid reaction, the later wash- $H_2O$  a fainter acid reaction. Animal tissue gives an alk. reaction. By warming the extd. plant tissue with  $H_2O$  an acid reaction was obtained which was strongest at 50–60°. S. believes that the reaction is as dependent on psychic stimuli as it is upon the temp. and that diseases are due to such reaction changes of the colloidal complexes.

C. C. DAVIS

**Invertase.** II. H. V. EULER AND K. JOSEPHSON. *Ber.* 56B, 1097–1103 (1923); cf. *C. A.* 17, 1251, 1647.—Invertase solns. prepd. by methods previously described were stable on standing 3 weeks, on concn. *in vacuo*, and were only slightly altered after pptn. with abs. EtOH and desiccation. The purest preps. obtained were closely related to proteins as shown by the positive biuret, xanthoprotic, and ninhydrin reactions, and by the N, S, and  $NH_2$  N content. The N and S content of the preps. increased with the increased activity on purification.  $NH_2$  N increased in proportion to the increase in total N (ratio 1:14–18). After 6 hrs. hydrolysis with concd. HCl, the  $NH_2$  N was 66% of the total N. Millon's reaction was not typical, the color produced being a yellow brown. The more crude preps. gave a positive Molisch test, but this became weaker as the purification progressed, indicating that carbohydrate is an impurity.

H. B. LEWIS

**Studies on enzyme action.** XXIV. The kinetics of the ester-hydrolyzing actions of some tissue and tumor extracts. KANEMATSU SUGIURA, HELEN M. NOYES AND K. G. FALK. *J. Biol. Chem.* 56, 903–20 (1923).—"The kinetics of the hydrolytic actions on glyceryl triacetate of exts. of the Flexner-Jobling rat carcinoma and the rat leg muscle were studied and interpreted on the basis of the monomol. reaction velocity equation, of Schütz's equation and of Northrop's equation. The general relations found were similar to those of other enzyme actions and are probably explainable on analogous grounds. A study of the hydrolytic actions on esters with different enzyme and substrate concns. showed that none of the theoretical equations was generally applicable, but that in certain series comparatively simple relations held within limits. It is extremely probable that enzyme actions take place in steps, that frequently the products of the reaction interfere with the actions, that a change in H ion concn. during the course of the actions complicates the interpretation, etc."

A. P. LOTHROP

**The preparation and properties of ovokeratin.** M. A. RAKUZIN. *J. Russ. Phys. Chem. Soc.* 49, I, 159–64 (1917).—The ovokeratin was prepd. by the method of Ladenburg (*Handwörterb. d. Chemie*, III, 2051–6) from the external membranes of hen eggs. The method consists of washing the membranes in warm (40°)  $H_2O$  until the filtered wash  $H_2O$  is protein-free, followed by 3 days' treatment with dil. NaOH, then for 3 days with dil. AcOH. The membranes of 50 eggs yielded 7 g. of grayish yellow keratin. The Na proteinate from the alk. treatment gave positive Adamkiewicz, Molisch, Pettenkofer and Ostromuiskii protein reactions. Since none of the animal and vegetable proteins ever gave the author the same four color reactions, he concludes that alkali exts. from egg membranes a hitherto unknown protein. Its  $[\alpha]_D = -4.87$ . The dil. AcOH ext. obtained above gave negative reactions with all of the usual protein color tests with the exception of Ostromuiskii's picramic acid test, which was positive, from which R. concludes that the AcOH ext. contains  $NH_2$  acids only produced by the preceding alk. hydrolysis. The  $[\alpha]_D$  of this ext. =  $-27.82$ . The ovokeratin obtained is extremely insol. In order to get a filterable sol. product it was necessary to hydrolyze it with concd.  $NH_4OH$  in a sealed vessel at 100° for 4 days. The product so obtained is not an  $NH_2$  keratinate, for it is pptd. by the removal of  $NH_3$  from its soln., and the dry residue after

evapn. is insol. The  $[\alpha]_D$  of this ammoniacal soln. is  $-36.79^\circ$ , while that of a similarly prepd. KOH soln. is  $[\alpha]_D = -38.96^\circ$ . The protein color reactions of the ovokeratin were positive to the following limits: biuret 1:1100; Millon 1:1100; Adamkiewicz 1:7700; xanthoproteic 1:3200; Molisch 1:800; Pettenkofer 1:1100; Ostromuiskenskii 1:1100. The Liebermann reaction was negative. The color reactions correspond closely to those of casein. The  $\text{NH}_3$  acid hydrolysis and analysis were not made, except that the large cystine content was shown by the presence of 2.30% S. The P content is practically nil.

W. A. PERLZWEIG

**The composition and properties of chondrin and chondroitin-sulfuric acid.** M. A. RAKUZIN AND EK. BRAUDO. *J. Russ. Phys. Chem. Soc.* **49**, 1, 200-7 (1917). Chondrin was prepd. from pig cartilage. In dil. aq. soln. its  $[\alpha]_D = -210.74^\circ$ . A new method of splitting off chondroitin- $\text{H}_2\text{SO}_4$  from chondrin was developed by means of adsorbing dil. solns. of chondrin on  $\text{Al}(\text{OH})_3$ . This process depends upon the initial concn. of the chondrin soln. Thus if to a 0.2% soln. of chondrin 10% by wt. of  $\text{Al}(\text{OH})_3$  is added and the mixt. allowed to stand for 24 hrs. the clear supernatant fluid above the sediment contains pure chondroitin- $\text{H}_2\text{SO}_4$  and it responds negatively to all protein color tests. With an initial concn. of 0.5% of chondrin the adsorbing process has to be repeated with a fresh portion of  $\text{Al}(\text{OH})_3$  before all protein reacting substances are adsorbed and pure chondroitin- $\text{H}_2\text{SO}_4$  remains in soln. After the first adsorption in this case protein-contg. cleavage products are present in the supernatant soln. With an initial concn. of about 1.0% of chondrin a simple irreversible adsorption occurs without any splitting. The purity of the chondroitin- $\text{H}_2\text{SO}_4$  was verified by the detn. of its S content. Its  $[\alpha]_D = -46.59^\circ$  in  $\text{H}_2\text{O}$ . The chondrin portion adsorbed by the Al sol which is free of chondroitin- $\text{H}_2\text{SO}_4$  is calcd. to have  $[\alpha]_D = 386.85^\circ$ . The adsorption-hydrolysis effect of  $\text{Al}(\text{OH})_3$  is claimed to be a new observation of great importance in the study of proteins.

W. A. PERLZWEIG

**Comparative studies on respiration. XXVII. The mechanism of oxidation in relation to chloroform anesthesia.** G. B. RAY. *J. Gen. Physiol.* **5**, 741-8 (1923); cf. *C. A.* **17**, 2589.—The action of  $\text{CHCl}_3$  on the oxidative mechanism of the cell is of a chem. nature. It acts either by catalysis or by the formation of a loose compd. with some portion of the system. A math. formula was developed to analyze the effects of  $\text{CHCl}_3$  on living and dead *Utrix* and on unsatd. org. acids. The same process takes place in all 3 cases. Lipoid soly. and changes produced in cell membranes will not explain these results.

CHAS. H. RICHARDSON

**Note on the purification and precipitation of casein.** J. H. NORTHKROP. *J. Gen. Physiol.* **5**, 749-50 (1928).—When casein is pptd. at its isoelec. point by acid, some of the protein is "denatured" and becomes permanently insol. If the final pptn. is made with alkali, a small excess has no effect on the casein. The casein is pptd. from milk by the method of Van Slyke and Baker (*C. A.* **12**, 1982). The ppt. is washed, suspended in  $\text{H}_2\text{O}$  and brought to  $p_H$  2.5-3.0 with  $\text{HCl}$ . The soln. is filtered till clear, which may require several days. It is then brought to  $p_H$  4.7 with  $\text{NaOH}$ . The ppt. is washed with  $\text{H}_2\text{O}$ , dried with  $\text{Et}_2\text{O}$  or kept as a fine suspension under  $\text{H}_2\text{O}$ . Casein prepd. in this way gives a practically water-clear soln. in alkali or acid. If the clear alk. soln. is pptd. with acid, a milky suspension results which cannot be centrifuged or filtered except near  $p_H$  4.7. This is due to the formation of a film of sol. casein salt about the casein particles, which prevents their coalescence. At  $p_H$  4.7, so little salt is formed that it no longer protects the particles and they coalesce. The soln. of isoelec. casein in alkali is purely a soly. effect.

CHAS. H. RICHARDSON

**The inactivation of trypsin. IV. The adsorption of trypsin by charcoal.** J. H. NORTHKROP. *J. Gen. Physiol.* **5**, 751-5 (1923).—Charcoal removes trypsin from soln. in amts. depending on the order in which the solns. are mixed. The reaction is not reversible and is almost independent of the  $p_H$  of the soln. Gelatin-treated charcoal does not remove trypsin from soln. The reaction between charcoal and trypsin is not analogous to that between trypsin and the inhibiting substance of serum or to the reaction between solid protein and pepsin or trypsin.

CHAS. H. RICHARDSON

**The influence of the hydrogen-ion concentration on the solubility of uric acid. II.** A. JUNG. *Helvetica Chim. Acta* **6**, 562-93 (1923).—Using, in addition to the four buffer solns. previously described (cf. *C. A.* **17**, 1253-4), 0.1 N KOAc + 0.1 N HOAc, 0.067 M  $\text{NaH}_2\text{PO}_4$  + 0.067 M  $\text{Na}_2\text{HPO}_4$  ( $p_H = 5.6-8.2$ ) (I), and 0.067 M  $\text{KH}_2\text{PO}_4$  and 0.067 M  $\text{K}_2\text{HPO}_4$  (II), J. from extensive measurements concludes that the soly. of uric acid (III) and mono-Na urate (IV) in salt solns. (of concns. not exceeding 1 mole per l.) follows the law of mass action, and is governed by the  $\text{H}^+$  concn. Similarly the solubilities of the various urates are detd. by the  $p_H$  established by their partial hydrolysis. The soly. of IV depends also on the cation present, being markedly decreased by  $\text{Na}^+$  and



$\text{Ca}^{++}$ , but unaffected by  $\text{K}^+$  and  $\text{Mg}^{++}$ . This effect, undoubtedly important in the organism, may be due to temporary adsorption complexes, not necessarily colloidal. The gradual change of dissociated uric acid and urates into the undissociated, more insol. acid tends to mask the strict accord of their soly. values with the law of mass action. Bacterial decompn. is especially marked in solns. of IV in  $\text{H}_2\text{O}$ , or in I, and is not inhibited by  $\text{CHCl}_3$ . IV is stable below  $p_{\text{H}} = 6$  in II. III is stable in acetate and borate solns., and below  $p_{\text{H}} = 7.5$  in II. Tables show the influence of standing, of  $\text{CHCl}_3$ , of coned. salts, KCNS and  $\text{CaCl}_2$ . I. P. ROLF

**Blood coagulation studies.** E. ZAK. *Arch. expl. Path. Pharm.* 97, 499-516 (1923).—Blood coagulation is not affected by pepsin or lab but trypsin, pancreatin, steapsin and diastase exert a marked inhibitory action. There is a direct parallelism between capacity for splitting fat and inhibition of coagulation. C. H. S.

**The polypeptide-splitting system of pancreatic press juice. The action of plant mucilage on the enzyme extract of the pancreas.** A. FODOR. *Fermentforschung* 6, 269-85 (1922).—The addn. of an ext. of Irish moss to the enzyme-substrate system increased the rate of hydrolysis, presumably by partially dehydrating the colloidal enzyme and thereby making more of its surface available to the substrate. By pptn. of the juice with acid a protein contg. P was obtained to which the ferment activity is attributed. R. L. STEHLÉ

## B—METHODS AND APPARATUS

STANLEY R. BENEDICT

**Measurement of lipoids in blood and tissues. III. A. New method of measurement of the unsaponifiable fraction and of the total fatty acids. B. Observations on the measurement of total lipid phosphorus in tissues.** P. LEMELAND. *Bull. soc. chim. biol.* 5, 110-24 (1923); cf. *C. A.* 15, 3854; 16, 4222.—A.—The Kumagawa-Suto method loses a small fraction of the fatty acids, and subjects the part measured to autoxidation. This is avoided as follows: Add serum or tissues removed immediately after death to 95% EtOH; after dehydration ext. 6 to 8 hrs. in the K.-S. app. with 95% EtOH. This gives total lipid. Evap. to dryness *in vacuo* the combined alc. exts. Saponify the residue: warm, refluxing for 2 hrs. with 25 cc. 2 N KOH (in 95% EtOH). Add to the same flask 40 cc. N HCl, 26.2 cc. 95% EtOH and 8.8 cc.  $\text{H}_2\text{O}$ , obtaining 100 cc. of 50% EtOH approx. 0.1 N alk. Warm 20 min., refluxing. Cool. Transfer quant. to a 500-cc. beaker, rinsing with 0.1 N KOH in 50% EtOH. Ext. with petroleum ether, flash pt.  $60^\circ$  (100, 50, 40, and 40 cc.). Add the petroleum ether fractions and wash with 50 cc.  $\text{H}_2\text{O}$ , which is added to the  $\text{H}_2\text{O}$ -EtOH portion to avoid loss of fatty acid. Evap. the petroleum ether fraction *in vacuo*, and est. the total unsaponifiable as previously described. To est. total fatty acid evap. the  $\text{H}_2\text{O}$ -EtOH fraction to  $1/2$  vol. on the water bath (removal of EtOH), transfer quant. to a beaker, just acidify with 1:3 HCl, ext. with 100, 50, and 50 cc.  $\text{Et}_2\text{O}$ , unite these exts. and evap. *in vacuo* after addn. of a few cc. pure EtOH. Dissolve in dry petroleum ether (flash pt.  $30^\circ$  to  $50^\circ$ ), filter through asbestos, and evap. on the elec. water bath. Dry the fatty acids 3 hrs. at  $65^\circ$  *in vacuo* of 30 min. Hg and in the presence of KOH. Weigh. Alternately, to reduce autoxidation to min. and permit further examn., add the  $\text{H}_2\text{O}$ -EtOH soln. to 50 cc.  $\text{H}_2\text{O}$ , bringing the total vol. to about 200 cc. (25% EtOH). Transfer quant. to a beaker and ext. 5 times with petroleum ether. Unite the fractions, evap. in a flask, and dry as above. B.—Comparison between  $\text{Et}_2\text{O}$  and  $\text{C}_6\text{H}_6$  as solvents for phosphatide removal indicates equal value for blood, but less for the former for tissues, on basis of P in ext. The difference is due to non-phosphatides except for the brain (sphingomyelin), so that, with this exception,  $\text{Et}_2\text{O}$  is regarded as the better solvent. A. T. CAMERON

**The presence in urine and biological liquids of certain drugs capable of affecting the measurement of urea as dixanthylurea.** R. FABRE. *Bull. soc. chim. biol.* 5, 125-32 (1923).—Certain drugs, as antipyrine and hypnotics of the barbituric series (e. g., veronal), can give xanthyl compds. under the same conditions as does urea. Since these are in part excreted unaltered in urine administration of sufficiently large doses may affect the measurement of urea as dixanthylurea. A. T. CAMERON

**Observations on Folin and Wu's method and the manganimetric modification for measuring small quantities of reducing sugar.** P. FLEURY AND L. BOUTROT. *Bull. soc. chim. biol.* 5, 149-52 (1923).—The color shade obtained by the addn. of phosphomolybdic reagent to the reduced soln. passes in some hrs. from blue with a slight greenish tinge to blue black. The color intensity varies equally. It attains its max. in less than 5 min., and diminishes at first rapidly, then more and more slowly, to a relatively stable state between 12 and 24 hrs. It seems to diminish more rapidly in tubes richest

in glucose, so that comparison tubes do not maintain the same ratio. The "permanganate index" is relatively very stable. (Apparently a comparison of Guillaumin's modification, *C. A.* 15, 1737, and that of Fonte's and Thivolle, *C. A.* 15, 3855.)

A. T. CAMERON

**Comparative value of the dialysis reaction (Abderhalden) and of the reaction to *B. coli*, as evidence of proteolysis.** E. WOLLMAN AND MME. E. WOLLMAN. *Bull. soc. chim. biol.* 5, 253-7(1923).—The latter method gives very regular results and is the more sensitive.

A. T. CAMERON

**Solubility of calcium oxalate in water in connection with the micromethods of calcium measurement in blood and body fluids.** W. MESTREZAT. *Bull. soc. chim. biol.* 5, 263-5(1923).—There is a double source of error in these micromethods: loss from soly. of  $\text{CaC}_2\text{O}_4$  and too great values from incomplete elimination of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . Corrections should be applied.

A. T. CAMERON

**Determination of the rate of digestion of protein.** A. FRIEDRICH. *Chem.-Zig.* 47, 265-6(1923).—A new method is described for detg. the rate of digestion of proteins, depending on the fact that during digestion protein changes from an insol. to a sol. substance. The liquid in which the protein is first suspended shows a change in concn. of substances in soln. which is a function of the extent of digestion, and this can be measured by means of a Löwe interferometer (cf. *C. A.* 15, 2398). When two successive readings are the same, it is assumed that all digestible protein is in soln. 2.5 g. of finely divided substance are shaken with 150-200 cc.  $\text{H}_2\text{O}$  and 10 cc. dil. HCl until interferometric detns. of 2 small filtered test portions at 1-hr. intervals show the same reading, 0.5 g. of a soln. contg. 0.5 g. pepsin is added, and the soln. made up to 250 cc. The soln. is kept at  $37^\circ$  and after shaking, a small portion (1 cc. is suggested) is filtered off at hourly intervals and tested in the interferometer. At the end of the reaction the dissolved protein is detd. by the following method: 2.5 cc. of filtered soln., 25 drops of concd.  $\text{H}_2\text{SO}_4$ , 5 drops of perhydrol, and a little  $\text{K}_2\text{SO}_4$  and  $\text{CuO}$  are heated to redness, cooled, a few drops of EtOH and perhydrol added and the mixt. is again heated to redness. The N is then detd. by the Kjeldahl method. Graphs show representative detns.

C. C. DAVIS

**The determination of the specific gravity of small quantities of urine.** ARNOLD KIRCH. *Med. Klinik* 17, 535; *Chem. Zentr.* 1922, IV, 867-8.—If the sample is too small for the urometer to float freely the following method can be used. If the vol. of unknown urine is  $n_1$  and into this is poured a urine of known d. until the total vol. reaches a vol.  $n$ , if the amt. of urine added is  $n_2$  and the d. of the mixt. is  $s_2$ , the desired d. is  $s_x$  and there follows the relation  $n_1s_x + n_2s_2 = Ns_2$ . From this:  $s_{x2} = Ns_2 / n_2s_1$  or  $s_x = (Ns_2 - n_2s_1) / n_1$ .

C. C. DAVIS

**Clinical and laboratory procedures in pediatrics.** A. LEVINSON. *J. Lab. Clin. Med.* 8, 664-78(1923); cf. *C. A.* 17, 2720.—A summary of methods used in the examn. of the spinal fluid.

E. R. LONG

**The Kottmann reaction for thyroid activity. Carbon dioxide in the tested serum.** SIERRE MORSE AND C. M. FITCH. *J. Lab. Clin. Med.* 8, 692-5(1923).—To 1 cc. of patient's serum add 0.25 cc. of 0.5% KI and 0.3 cc. of 0.5%  $\text{AgNO}_3$ . Shake and expose 5 min. to a 500-watt Mazda lamp at a distance of 25 cm. Add 0.5 cc. 0.25% hydroquinone. Note the color changes. The  $\text{CO}_2$  content of the serum plays an important role in the color changes following the addition of hydroquinone; a decrease in the content usually accelerates the color change. Thus in serums losing  $\text{CO}_2$  the most rapid color change took place at the surface. These results indicate that conclusions based on the Kottmann reaction must be revised with consideration of the  $\text{CO}_2$  content of the blood.

E. R. LONG

**A note on the detection of coagulable protein in feces.** ROBERT COOPE. *Lancet* 1923, I, 1311-2.—In order to obtain a clear filtrate from feces upon which a test for protein may be made, half saturate fecal emulsion with  $(\text{NH}_4)_2\text{SO}_4$  and filter. Soap gels are thrown out and filtration is thus facilitated. Globulins are of course also pptd., but there is no evidence that globulins may occur in feces in the absence of albumin. The usual tests for albumin, such as the heat coagulation and sulfosalicylic acid tests, may be employed upon the filtrate. By this method the min. amts. of blood serum added to 100 g. of feces which could be detected ranged from 0.125 to 0.5 cc. In infants, particularly in diarrhea, a positive result is common. In adults the presence of fecal albumin is almost invariably due to bleeding or exudation.

E. R. LONG

**The Ostromuilenaskii reaction with proteins.** M. A. RĂZUIN. *J. Russ. Phys. Chem. Soc.* 49, I, 164-9(1917); cf. *C. A.* 11, 3043.—The Ostromuilenaskii picramic acid reaction (O.R.) was found to be positive with all animal and vegetable proteins with the exception of elastin; the failure of this to react is ascribed to its extreme insoly.

Proteinates combined with cations react similarly with the exception of  $\text{NH}_4$  proteinates. Of the 8 protein color reactions (ninhydrin not included) applied to free  $\text{NH}_4$  acids the O.R. alone was positive, but it was negative with the  $\text{NH}_4$  salts of the  $\text{NH}_4$  acids and where the  $\text{NH}_4$  group was combined with  $\text{HCl}$  or other acids. Only glycocoll, leucine, aspartic acid and asparagine were studied. The O.R. is sp. for the free  $\text{NH}_4$  group in protein and in its cleavage products. The protein nature of agar-agar, purified pepsin and trypsin is denied by R. on the basis of negative O.R. Picramic acid is recommended as a valuable reagent in the study of proteins. W. A. PERLZWEIG

**The titration of organic acids (in the urine) in acidosis by the method of Van Slyke and Palmer.** M. LABBÉ, H. BITH AND F. NEPVUX. *Presse med.* 31, 505-6(1923).—The method of Van Slyke and Palmer for the detn. of org. acids in the urine (*C. A.* 13, 2892) is described in detail and discussed. The values obtained by this method depend on the indicator employed. Thus when dimethylaminoazobenzene (end point at  $p_H$  4) was used instead of Orange IV (tropheolin OO, end point at  $p_H$  2.7) the figs. obtained were consistently approx. 30% lower with the former than with the latter. The curves of excretion of acetone bodies and of org. acids in diabetic acidosis were fairly nearly parallel; however, the org. acids curve for any given period was more const. than the acetone bodies curve. The org. acids curve in these cases also ran parallel to the titratable acidity,  $\text{NH}_4$  acids and  $\text{NH}_4$  excretion curves. In fasting normal subjects the excretion of org. acids was within normal limits, while the excretion of acetone bodies was greatly increased. W. A. P.

**Ideas concerning applications of the Abderhalden reaction for testing for the presence of definite cell varieties.** E. ABDERHALDEN. *Fermentforschung* 6, 357-8 (1923); cf. *C. A.* 17, 778.—It is suggested that use be made of the reaction to det. the completeness of removal of the thyroid and for analogous purposes. R. L. STIGHELE

**Determination of volatile fatty acids in bacterial cultures.** A. I. VIRTANEN. *Medd. Centralanstalt. försöksväsendet jordbruks.* No. 242(1923).—Small amts. of lactic acid pass over with steam especially with strong solns. Results obtained at ordinary pressure are as accurate as those obtained by vacuum steam distn. No decompn. of proteins or fats took place in a distn. carried out at ordinary pressure. Volatile acids distil much more readily from solns. contg. salt than from their solns. in pure water, but lactic acid passes over in fair amts. from strong saline solns. The lactic acid which passes over with steam distn. must be taken into account; it may be estd. by evapp. the distillate to a small bulk, acidifying and redistg. with steam, as the amt. passing over the second time will be so small as to be negligible. C. O. SWANSON

#### C—BACTERIOLOGY

A. E. BALLS

**Formation of fat and lipid substances. I. Influence of the nature of carbohydrate in culture fluid on the content of fatty substances in the tubercle bacillus, and the properties of these substances.** E. F. TERROINE AND J. E. LOBSTEIN. *Bull. soc. chim. biol.* 5, 182-99(1923).—Exhaustive extn. by boiling  $\text{EtOH}$  in a Kumagawa-Suto app. does not remove from powdered tubercle bacilli the whole fat content; 2.5 to 3 g. fatty compds. per 100 g. bacilli remain. Under identical conditions of culture, tubercle bacilli of bovine origin contain more fat than those of human origin. In both strains lipid content diminishes to 60% if glucose is substituted for glycerol as ternary aliment, C content and other conditions remaining identical. The unsaponifiable portion, treated by alc. soln. of digitonin, yields a cholesterol complex, 0.16-0.45% giving marked Salkowski and Liebermann-Burchard reactions. Its ratio to total lipids is very constant for bacilli of the same origin: higher (1.8%) for bovine than for human (1.3%). Where glucose or glycerol is used, the fatty acids formed have approx. the same m. p. but with glycerol the I-index is a little higher. The protein content is higher with glucose than with glycerol (11.6 and 8%). A. T. CAMERON

**The production of various organic compounds by mold fungi with deficiency of oxygen.** S. KOSRYCHEV AND M. AFANASSIEVA. *Jahrb. wiss. Botan.* 60, 628-50; *Chem. Zentr.* 1922, III, 391-2; cf. *C. A.* 15, 1550.—Cultures of *Aspergillus niger* always contain ymase with tartaric acid, lactic acid, glycerol, mannitol and quinic acid, and produce  $\text{EtOH}$  when O is excluded and the nutrient soln. has a neutral reaction. A weak acid reaction greatly hinders the formation of  $\text{EtOH}$ . When O is excluded sugar-like substances are always formed in the nutrient soln. It is concluded that the above-named N-free nutrients are consumed through the intermediate stage of sugar. Peptone cultures of *Aspergillus niger* are ymase-free and produce no  $\text{EtOH}$  when O is excluded, even after the addn. of sugar. From this it is assumed that "sugar respiration" and

"protein respiration" represent 2 different chem. processes. Sugar cultures of *Aspergillus niger* consume considerable amts. of sugar when O is excluded without formation of EtOH. Cultures of *Penicillium glaucum* also form EtOH when the medium has a neutral reaction but only 0.1 the amt. that *Aspergillus* forms. Much greater quantities of EtOH are produced by *Penicillium* which has been cultivated on powdered bread.

C. C. DAVIS

**Catalysis of hydrogen peroxide by bacteria.** D. RYWOZ. *Przeglad epidemjol.* 1, 525-9; *Ber. ges. Physiol.* 12, 297; *Chem. Zentr.* 1922, III, 274.—Investigations of optional anaerobic bacteria showed that life in an O atm. is necessary for the formation of a catalase. The catalase formed protects the bacteria against not too great amts. of  $H_2O_2$ .

C. C. DAVIS

**Aerobic decomposition by mold fungi.** N. I. KOSIN. *Nachr. Phys.-Chem. Lomonossow-Ges. Moskau* 2, No. 1, 57-98(1921); *Chem. Zentr.* 1922, III, 874.—Mold fungi, especially *Cladosporium*, decompose cellulose energetically in the presence of air and mineral acids. Hexose is first formed and is in turn decompd. to  $CO_2$ . In expts. approx. 25% of the cellulose was decompd. in 256 days. The saccharification was due to an enzyme which was isolated by K. A similar decompn. occurred in nature in the summer months, with similar formation of sugar. Exptl. data are tabulated. C. C. DAVIS

**Variation in results obtained with bacteriological sugars.** G. MACKEY. *Proc. 7th Indian Sci. Cong.* 1921, clvii.—If the complete reactions toward sugars of a given organism are to be obtained, that organism should be transplanted to them from an actively growing young culture in a fluid medium. The results are not so complete or so certain if the planting is done directly from an agar culture or a suspension made from an agar culture. Inattention to this point may be the cause in some cases of rejection of sugars as impure or of the view that the strain is a new one. C. C. DAVIS

**Production of oxidizing enzymes.** O. FERNÁNDEZ AND T. GARMÉNDA. *Anales soc. españ. fis. quim.* 21, 166-80(1923).—Cultures of *B. coli* were grown under both aerobic and anaerobic conditions in different mediums contg. various sugars, polyalcohols, and amino acids, and the relative amts., if any, of peroxidase and catalase formed were detd. From the widely divergent results obtained no definite conclusions can be drawn.

L. E. GILSON

**Reducing action of microorganisms on ammonium molybdate.** V. E. LEVINE AND H. M. JAHR. *Abstracts Bact.* 5, 4-5(1921).—Bacteria growing in peptone broth contg.  $(NH_4)_2MoO_4$  reduce that compd. with the production of an intense blue color. Sterile dextrose peptone broth produces this reduction at a temp. of 37.5° but not at room temp. Peptone broth contg. 1% lactose and 1%  $(NH_4)_2MoO_4$  is reduced only in the presence of microorganisms. No relationship exists between reduction and fermentation. Living yeast cells also produce the reduction. Both bacteria and yeast secrete reductase as an endocellular enzyme; the reduction is due partly to this enzyme and partly to the metabolic products of the organisms. Low concns. of  $(NH_4)_2MoO_4$  do not retard bacterial growth; the degree of retardation, or even complete inhibition, produced by a relatively high concn. (1%) varies with the species. J. S. HEPBURN

**Influence of carbohydrate on the nitrogen metabolism of bacteria.** L. F. RETTGER. *Abstracts Bact.* 5, 3-4(1921).—The retarding or preventive influence of a utilizable carbohydrate on N metabolism may be materially modified when appreciable amts. of a buffer like  $K_2HPO_4$  are present in the medium. JOSEPH S. HEPBURN

**Separation of bacteria by filtration with Zsigmondy-Bachmann membrane filters.** H. MEYERINCH. *Z. Hyg. Infektionskrankh.* 97, 116-36(1922).—The Zsigmondy-Bachmann filters (cf. Ger. pats. 329,060 and 329,117; J.), if suitably selected, rapidly yield a germ free liquid, and moreover, the ease with which the residues are removed from the filters renders them especially suitable for sepg. bacteria from such liquids as water and urine. Their low adsorptive capacity renders them suitable for filtering colloidal solns. A lower grade of porosity is necessary to prevent propagation of individual species of bacteria through the filters than for simple filtration. By employing filters of low porosity, propagation of bacteria through the filters is entirely prevented and these can be used with safety for the rapid production of germ-free drinking water.

J. S. C. I.

**The coagulating enzyme of the yeast cell.** A. M. NASTYUKOV AND N. S. PYATNITZKI. *J. Russ. Phys. Chem. Soc.* 49, I, 183-6(1917).—N. had previously shown that the living yeast cell is capable of coagulating yolk proteins in a slightly alk. medium. In the present article it is shown that filtered yeast maceration juice, prepd. by Lebedev's method, contains an enzyme or enzymes which coagulate yolk proteins. This enzyme is thermostable and is present in the filtrate from boiled maceration juice. A specially prepd. yolk nutritive medium, devised by M. M. Nastyukov, was used. 0.5 cc. of the

maceration juice added to 10 cc. of sterile medium and kept at 35° was sufficient to show coagulation, which became visible after 3 hrs. and was complete at the end of 5 days. The elementary analysis of the purified coagulum showed that the latter is quite different from unchanged yolk vitellin and from the usual peptic cleavage product of vitellin. This circumstance leads the authors to believe that the coagulating and proteolytic actions of the yeast cell depend upon the presence of at least 2 distinct enzymes.

W. A. PERLZWEIG

**Coefficients of utilization and rate of growth in fungi.** CH. KILLIAN. *Compt. rend.* 176, 1828-30(1923).—*Penicillium glaucum* and *Cladosporium herbarum* were grown in the culture medium of Czapek without Zn, contg., as a source of N, 0.5% of  $(\text{NH}_4)_2\text{SO}_4$  or other materials in amts. to furnish the same quantity of N, namely,  $\text{NH}_4\text{NO}_3$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$ , asparagine and urea. With both fungi the coeff. of utilization (*U*) and the rate of growth (*G*) were greatest when the source of N was asparagine and least with urea. With  $\text{NH}_4$ , K and Na nitrates or  $(\text{NH}_4)_2\text{SO}_4$  as sources of N there was a general agreement in both figures. *Cladosporium* showed in each case a higher *U* and with but one exception a lower *G* than *Penicillium*. Increase in the acidity of the medium causes a decrease in both figures. When the concn. of the N was decreased to 0.05%, *U* remained the same but *G* was lowered by more than one-half with *Penicillium*, and was lowered in a less degree with *Cladosporium*. The effect of different sources of C was tested by using arabinose, glucose, xylose, levulose and galactose, resp., in the culture medium. With  $(\text{NH}_4)_2\text{SO}_4$  as a source of N, *U* is increased for both fungi in the order in which the sugars are named. The findings reported in this paper compared with those detd. for *Aspergillus niger* (cf. Terrline and Wurmser, *C. A.* 16, 732, 3102, 3931) show fundamental differences between the fungi. L. W. RIGGS

Effects of isolation on *Oidium lactis* (BITTING) 12.

#### D—BOTANY

B. M. DUGGAR

**Growth and transport of organic substances in bitter cassava (*Manihot utilisima*).**

T. G. MASON. *Sci. Proc. Roy. Dublin Soc.* 17, 105-12(1922). E. J. C.

**Irritation and reaction to irritation in the vegetable kingdom.** FELIX RAWITSCHER. *Naturwissenschaften* 11, 491-7(1923).—A review with a bibliography. C. C. DAVIS

**The importance of calcium to plants.** D. PRIANISCHNIKOW. *Ber. botan. Ges.* 41, 138-44(1923).—Plant growth is checked and phenomena of disease are noted when Ca salts are available to only a portion of the root system. Dil. solns. of salts of bivalent metals increase the acid resistance of plant cells.  $\text{Ca}^{++}$  exerts the strongest, and univalent cations the weakest, antitoxic action against  $\text{H}^+$  ions. No specific action of the anions was observed. ARTHUR LOCKE

**Phenomena of optical sensitization in plants.** F. SCHANZ. *Ber. botan. Ges.* 41, 165-70(1923).—The toxic effects of ultra-violet light upon plant plasma are realized at longer wave lengths in the presence of sensitizers. Erythrosin and eosin are not poisonous to the plant in the dark but cause death in the light. Methylene blue is not toxic. ARTHUR LOCKE

**The potassium and iodine content of the Black Sea alga, *Cystoseira barbata*.** V. SHKATELOV. *J. Russ. Phys. Chem. Soc.* 49, 122-30(1917).—The air-dried alga yielded 14.5% ash. The compn. of the ash in % was:  $\text{CaSO}_4$ , 0.6337,  $\text{K}_2\text{SO}_4$ , 28.10,  $\text{Na}_2\text{SO}_4$ , 1.3335,  $\text{MgSO}_4$ , 0.7482,  $\text{NaCl}$  26.0548,  $\text{NaI}$  0.0572,  $\text{NaBr}$  0.8095, insol. 41.38, org. substances and C 2.76. On comparison with the ash compn. of Western European algae and kelps the following differences are pointed out: the ash of *Cystoseira* contains no carbonates, has a greater  $\text{SO}_4$  content, and shows a much smaller I content, which is replaced by an excess of Br. W. A. PERLZWEIG

**The determination of free amino groups in vegetable proteins by Van Slyke's method.** A. I. OPARIN. *J. Russ. Phys. Chem. Soc.* 49, 1, 266-71(1917).—Cryst. preps. of globulins were made from the seeds of a number of plants by T. B. Osborne's method (*Am. Chem. J.* 14, 663(1892)). The % of free  $\text{NH}_2$  N as obtained by Van Slyke's method of the total N (Kjeldahl) of the resp. globulins is as follows: cucumber 2.69; watermelon 2.67; musk melon 2.68; egg plant 2.66; squash, edible 2.66; squash, decorative 2.66; hemp seed 2.41; cottonseed 2.42; fir seed 1.87; poppy seed 2.48. Attention is called to the close agreement among these figures. W. A. PERLZWEIG

**Conservation of seeds in inert gases.** J. HOUDAS. *Compt. rend.* 176, 1407-9(1923).—Under ordinary conditions seeds of *Gerbera jamesoni* and of its hybrids preserve their germinating vitality but a few weeks. Seeds were preserved each year from 1912 to 1922 in atms. of H and of  $\text{CO}_2$ , whereupon their germinative ability was unimpaired

during periods of 1 to 11 years. Similar results were obtained with other short-lived seeds.

**Supposed reserve dextrins of monocotyledons.** H. COLIN AND H. BELVAL. *Compt. rend.* 176, 1493-5 (1923).—The work of Leclerc du Sablon (1898-99) showing reducing and non-reducing sugars, dextrins and starches in the bulbs of *Hyacinthus orientalis* for each season of the year is questioned. The reserve carbohydrate in the bulb is composed exclusively of starch and a sol. levogyrous levulosan present in sufficient amt. to communicate a decided viscosity to the juice. The bulb contains no gums of the galactopentosan group. Several other monocotyledons show analogous compus. Levulosans have been mistaken for dextrins. In *H. orientalis* dextrin never exists in appreciable amts. along with starch.

**Variations on some of the carbohydrate reserves in *Mercurialis perennis*.** L. P. GILLOV. *Compt. rend.* 176, 1657-9 (1923); cf. C. A. 17, 1492.—The annual cycle of the plant may be divided into 5 periods: (1) uniquely subterranean life extending from the fall of the leaves to beginning of spring vegetation, Dec.-Mar.; (2) rapid aerial growth, flowering and fruiting, Mar.-Apr.; (3) period of assimilative activity, without the formation of new organs, May-Aug.; (4) continuation of the period of assimilative activity, with the appearance of subterranean ramifications, Aug.-Sept.; (5) decline of aerial vegetation and development of subterranean roots, Oct.-Nov. Dets. of various carbohydrates during each of the 5 periods above mentioned gave results in parts per 100 of fresh organ as follows: (1) Starch varies slightly, approaching a min. of 3 to 4; maltose is nearly const. at about 1; and sucrose, which was at a max. of 4 at the beginning of the period, diminishes with the increase of underground tissue. (2) Starch remains at a min.; maltose diminishes to 0.5; and a further amt. of sucrose disappears. (3) From the beginning of this period starch accumulates; maltose increases; but sucrose diminishes to 1. (4) At the end of this period starch attains a max. of 6 in the rhizomes and 13 in the roots; maltose increases to 2; and sucrose increases to more than 2. (5) About half of the reserve starch disappears; maltose diminishes to one-third; and sucrose doubles in amt.

**Biochemical study of the composition of *Monotropa hypopitys* L.** Discovery of a new glucoside, monotropein. MARC BRIDEL. *Compt. rend.* 176, 1742-4 (1923); cf. C. A. 16, 1451, 1970, 4246.—This plant, which has no chlorophyll, was extd. the day after collection with boiling alc. and a final aq. ext. of the product was used for the tests. This aq. ext., of which 100 cc. corresponded to 100 g. of the fresh plant, showed a rotation of  $3^{\circ}48'$  and an initial amt. of reducing sugar equal to 0.947 g. per 100 cc. After invertase had acted on it 15 days the rotation was  $6^{\circ}7'$  and the reducing sugars were 2.673 g. These figures give an index of 745, which indicates that *M. hypopitys* contains a sugar not sucrose. After emulsin had acted 4 months the rotation was  $-3^{\circ}18'$  and the reducing sugars were 3.359 g. The glucoside, for which the name monotropein is proposed, was extd. from 5200 g. of the plant, 2 g. of pure colorless crystals being obtained. Monotropein is acid to taste, evolves  $\text{CO}_2$  from  $\text{NaHCO}_3$  and is levogyrous.  $[\alpha]_D^{20} = -130.44^{\circ}$ . It is hydrolyzed by  $\text{H}_2\text{SO}_4$  and by emulsin, giving a blue soln. which is decolorized by  $\text{Pb}(\text{AcO})_2$ . The blackening of *M. hypopitys* on drying is caused by monotropein, the same as the action of aucubin in plants of the genus *Melampyrum*.

**Chemical composition of *Monotropa hypopitys* L.** A. GOKIS. *Compt. rend.* 176, 1826-8 (1923); cf. preceding abstract.—The work of Bridel is confirmed, and the following new information is given with reference to this plant. If *Monotropa* is treated with boiling alc. and the alc. distd. off the aq. residue is rich in phenols, largely gallic acid. The aq. residue deprived of its phenols by extn. with  $\text{Et}_2\text{O}$  or  $\text{EtOAc}$  yields 2 glucosides, one of which consists of whitish plates, m.  $131^{\circ}$ , and the other is the monotropein with characters indicated by Bridel. It reduces Fehling soln., commences to turn brown at  $160^{\circ}$  and m.  $174-5^{\circ}$ . Its rotatory power is  $[\alpha]_D^{20} = -128.32^{\circ}$ . Many other expts. with this plant are described.

**Experimental study of the reddening of cherries.** FERNAND OBATON. *Compt. rend.* 176, 1824-5 (1923).—A refrigerating closet was devised so that branches carrying fruit could be inclosed in the closet without sepn. from the tree, and the air circulation, temp. and light could be controlled. The results proved that the reddening of cherries depends on the temp., and that the light has no direct action on this phenomenon. A study of the respiratory quotient showed that the reddening fruits are the seats of a fixation of  $\text{O}_2$ .

**The ash content of the juice of rhubarb.** LEIF GROGAARD. *Tidsskrift for Kemi og Bergvaesen* 2, 128-31 (1922).—Investigations were made at the Technical High school of Norway. In 30 samples of 20 rhubarb plants from 15 different places the sp. gr. of the juice varied from 1.0136 to 1.0271 and its ash content from 0.486 to 1.653,

av. 0.787%. The amts. of acid used to neutralize the juice ash, detd. by heating with an excess of 0.1 N  $\text{H}_2\text{SO}_4$  on a boiling water bath for 1 hr. and retitrating, varied from 3.56 to 21.50 cc. per 100 g. juice, av. 8.83 cc., or calcd. per 1 g. ash: 7.11–13.01, av. 10.79 cc. 0.1 N  $\text{H}_2\text{SO}_4$ . The spring samples showed less of ash and a lower alkalinity than the autumn samples.

CHR. H. A. SYVERTSEN

**Exosmosis in relation to injury and permeability.** W. J. V. OSTERHOUT. *J. Gen. Physiol.* 5, 709–25(1923).—"The time curve expressing the increase in the permeability of *Nitella* during the process of death is practically the same whether derived from measurements of exosmosis or of elec. resistance." C. H. R.

**The penetration of dyes as influenced by hydrogen-ion concentration.** M. IRWIN. *J. Gen. Physiol.* 5, 727–40(1923); cf. *C. A.* 17, 406.—The sap from *Nitella* cells which have been placed in buffer solns. at  $p_H$  9 shows an increase from  $p_H$  5.6 to 6.4 when death of the cell occurs. When living cells are placed in 0.002% brilliant cresyl blue soln., the rate of penetration and final equil. attained by the dye increase with the increase of  $p_H$ . This is attributed to an increase in the active protein or other amphoteric electrolyte in the cell.

CHAS. H. RICHARDSON

**Theory of regeneration based on mass action.** JACQUES LOEB. *J. Gen. Physiol.* 5, 831–52(1923).—This confirms previous expts. (*C. A.* 14, 758, 2653) in showing that equal masses of isolated *Bryophyllum* leaves regenerate under equal conditions and time equal masses (in dry wt.) of shoots and roots. **Theory of geotropism based on mass action.** *Ibid.* 853–63.—Geotropic curvature in *Bryophyllum* is a function of the mass action of the material sent into the basal part of the stem. The material sent by the leaf to the apical part of the stem does not lead to the same curvature. C. H. R.

Relation of acidity to carbon dioxide adsorption by certain gels and plant tissues (CAREY) 2.

## E—NUTRITION

PHILIP B. HAWK

### NORMAL

**The vitamin requirements of certain yeasts and bacteria.** L. FREEDMAN AND C. FUNK. *Proc. Soc. Exptl. Biol. Med.* 19, 198–201(1922).—Beef-heart infusions and autolyzed yeast solns. were subjected to fractional adsorption by means of fuller's earth and norit charcoal; the adsorbents were extd. with baryta and glacial  $\text{AcOH}$ , resp., and the influence of these exts. was tested on the growth of yeast cells and streptococci; substances were present which stimulated growth and which belonged to vitamins of the water-sol. B type. A study of protein hydrolyzates lead to the belief that their growth-stimulating action is due to a vitamin-like substance present as an impurity.

C. V. B.

**The almond as a source of vitamin A.** M. S. ROSE AND G. MACLEOD. *Proc. Soc. Exptl. Biol. Med.* 19, 391–3(1922).—Young rats failed to grow on a diet of almond meal, salt mixt., and a little starch, the almonds constituting 81% of the diet. A press cake contg. 35% fat gave slightly better results as a substitute for almond meal. The rats grew well for 5–6 weeks when given a basal diet deficient in vitamin A but contg. 3% of the bleached-almond diet. Almonds seem to be fairly rich in vitamin A, but to contain some harmful substance which prevents growth when given in large amts.

C. V. B.

**Vitamins and iron metabolism in growing individuals.** K. HARAMAKI. *Biochem. Z.* 134, 354–9(1922).—A small growing dog was used. The body of the growing animal can retain Fe on a vitamin-free diet. Nevertheless, the addn. of vitamins to the diet seemed to favor retention of Fe, if excess over that fed in the preliminary period was given. Vitamins are more important in Fe assimilation during growth than when the adult size is reached.

F. S. HAMMETT

**Studies in the physiology of vitamins. III. A comparison of the effects of feeding extracts of muscle and of yeast, respectively. IV. Parenteral administration of products containing vitamin B. Mammalian experiments.** G. R. COWGILL. *Proc. Soc. Exptl. Biol. Med.* 19, 282–4(1922).—Dogs were given a diet lacking in vitamin B. Ext. of yeast vitamin (Harris) given by stomach tube caused a prompt recovery of appetite which lasted from 4 to 19 days. Com. ext. of beef muscle (Liebig's) had no such effect. A neutral aq. protein-free soln. of vitamin ext. given intravenously promptly restored appetite and was followed by a complete cessation of nervous symptoms associated with the lack of vitamin B. Cf. following abstr.

C. V. B.

**An improved procedure for metabolism experiments.** G. R. COWGILL. *J. Biol. Chem.* 56, 725–37(1923).—"The first important principle upon which the new procedure

is based is that the diet for the dog shall consist of a mixt. of isolated food substances which, when fed, will supply the body with everything that is necessary for proper nutrition (except vitamin B), or which lacks only one thing (other than vitamin B) namely, the variable under consideration. The second important principle followed is that the vitamin B shall be administered *apart* from the food mixt. above mentioned." The diet is calcd. on a kg. of body wt. basis and for dogs weighing over 7 kg. is constituted as follows per kg. of body wt.: 80 cal.; 0.8 g. of protein N; from 32 to 36 cal. in the form of fat, this foodstuff in g. constituting not over 25% of the whole; 0.4 g. of agar or bone ash; 0.2 g. of salt mixt.; and either 7% of butter fat or 2% of cod-liver oil as a source of vitamin A (the former preferred as dogs in general do not like cod-liver oil). The compn. of the salt mixt. (Karr's) is as follows: NaCl 10 g., Ca lactate 4 g., Mg citrate 4 g., Fe citrate 1 g., Lugol's soln. a few drops; this mixt. is fed with bone ash which furnishes the phosphate needed. Casein is recommended as the protein and sucrose as the carbohydrate most desirable. Any concd. form of vitamin B may be used but must be standardized by feeding tests. If "Yeast Vitamin Powder (Harris)" is used, 60 mg. per kg. of body wt. per day should be administered *apart* from the rest of the food in a gelatin capsule. The energy factor has been shown to have an important influence on appetite and the plan of feeding described furnishes only enough cal. to permit maintenance in adult animals or sufficient to allow a slight increase in body wt. in growing dogs. This procedure has proved highly successful and its importance should not be overlooked by those who wish to make their exptl. animals eat voluntarily every bit of food offered during the course of long metabolism expts. When agar is preferred for roughage the following new salt mixt. devised by C. may be used on the basis of 0.3 g. per kg. of body wt.: NaCl 38; Mg citrate 32.5;  $\text{KH}_2\text{PO}_4$  12.2;  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  7.8; KCl 7.0; Fe citrate 1.8; KI 0.5%. This mixt. supplies in the food daily an amt. of each substance equal to or slightly in excess of that normally eliminated by the kidneys in 24 hrs. and also offers to the body certain constituents in fairly normal ratios to others, e. g., Na to K. The food is prepd. without the use of  $\text{H}_2\text{O}$  and does not develop an odor due to rancid fat nor dry out even when a large amt. is prepd. at one time. A typical kg. unit of casein food has the following % compn.: casein (12.7% N and 81.9% pure) 37.6; sucrose 34.9; lard 17; butter fat 7; bone ash 2.3; salt mixt. 1.2; 10.74 g. of this mixt. has a cal. value of 80. One dog was fed this diet with no failure of appetite whatever for 150 days so that monotony of diet cannot be regarded *per se* as a cause of failure of appetite and the use of meat in feeding dogs is quite unnecessary. When a dog has lost its appetite because of lack of vitamin B, the desire to eat may be restored within 1-2 days by giving a single large dose of this dietary essential. Cf. preceding abstr.

A. P. LOTHROP

The presence of a yeast growth-promoting vitamin in cane-sugar. CASIMIR FUNK AND LOUIS FREEDMAN. *J. Biol. Chem.* 56, 851-60 (1923).—Ordinary cane-sugar contains a vitamin-like substance which promotes the growth of yeast cells and which is probably identical with vitamin D, the presence of which F. has always maintained is necessary for the growth of the yeast cell (a view not shared by other investigators). This vitamin-like substance can be removed by shaking the sugar soln. with fuller's earth and recrystg. from alc. or by direct crystn. from alc. and this procedure should always be followed when the sugar is to be used in a synthetic medium. Although yeast cannot grow in an absolutely pure medium devoid of vitamin D, the amt. of this substance carried over by the inoculation is often enough to promote growth and hence give misleading results. The source of the inoculating cells must always be considered as yeast grown in a synthetic medium poor in vitamin D cannot be used as a good source of vitamin B for animal feeding expt. as yeast cannot synthesize vitamin B in the absence of vitamin D. The findings "emphasize once more the evident importance of the 'infinitely little' in nutritional expts.; and that com. pure substances, like cane-sugar, should not be used in expts. in nutrition without further purification." A. P. L.

Growth-promoting substances of bacterial origin. S. R. DAMON. *J. Biol. Chem.* 56, 895-902 (1923).—Albino rats were fed a diet adequate except for vitamin B and, after a decline in wt. had set in, the desiccated bacteria were added to the basal ration replacing 5% of the starch. 5% of a spore-forming aerobic organism, *B. adhaerens*, and of a mucoid organism, Friedlander's bacillus, failed to supply the deficiency of vitamin B in the otherwise adequate diet. 5% of the mucoid organism, Pfeiffer's bacillus, and of an acid-fast organism, *B. timothy* (the timothy grass bacillus of Moeller), maintained the rats at a const. wt. or induced rapid growth. 10% of the *B. timothy* induced rapid and continuous growth. D. "desires to take strong exception to the use of the term 'vitamin' as applied to any growth-stimulating substance of bacterial origin until such substance has been subjected to the biol. test. In the work reported certain or-



ganisms to which growth-promoting properties have been attributed have been subjected to such a test with widely divergent results. In the case of the Friedlander's and Pfeiffer's bacilli, both members of the same group of organisms, no explanation of the discordant results presents itself."

A. P. LOTHROP

#### ABNORMAL

**Spontaneous cure of rickets in rats.** A. F. HESS, L. J. UNGER AND A. M. PAPPENHEIMER. *Proc. Soc. Exptl. Biol. Med.* 19, 236-8(1922).—Rats fed a rickets-producing diet contg. an inadequate amt. of P showed X-ray signs of rickets after 32 days; after 48 days the radiographs showed healing, and after 74 days no evidences of rickets were found at necropsy. With a practically stationary weight over a long period of time, the P requirement for the building up of new tissue is greatly reduced and the bone is enabled to recalcify. II. The prevention of rickets in rats by light rays. *Ibid* 238-9.—In white and black rats the skin pigment retarded the rays which are effective in rickets.

C. V. B.

**Calcium phosphate metabolism showing the prevention of rickets by feeding clear grades of flour.** J. F. McCLENDON. *Proc. Soc. Exptl. Biol. Med.* 19, 356-9(1922).—Rats were given diets contg. flour of varying P contents. After 10 days the Ca-P metabolism was detd. Rats having an intake of 4.2-5.1 mg. of P and 21.2-23.7 mg. of Ca, with an output of 3.1-3.5 mg. of P and 19.7-22.7 mg. of Ca developed rickets. Rats free from rickets ingested 20-25 mg. of P and 46-48 mg. of Ca, with an output of 13.8-15.8 mg. of P and 38.1-32.7 mg. of Ca. The rachitic rats received thrice milled flour; those remaining healthy received either twice milled or Graham flour. The analytical methods are given in detail.

C. V. B.

**Diagnostic value of phosphate metabolism in experimental rickets.** J. F. McCLENDON. *Proc. Soc. Exptl. Biol. Med.* 19, 412-3(1922).—From a study of 150 rats which were fed a rachitic diet, the following rachitic index was developed.  $RI = \text{increase in body weight} \times 0.0022 - (\text{P retention} - 2)$ . If  $RI$  is positive the rat has rickets, if negative the rat is normal. A low P intake has an associated low P and Ca retention and signs of rickets. A low Ca intake causes osteoporosis without influencing the P metabolism or causing rickets.

C. V. B.

#### F—PHYSIOLOGY

ANDREW HUNTER

**Basal metabolism in relation to body surface at different ages with special reference to prematurity.** F. B. TALBOT AND W. R. SISSON. *Proc. Soc. Exptl. Biol. Med.* 19, 309-11(1922).—The av. heat production per sq. m. of body surface of 22 premature infants was 597.3 cal. in 24 hrs., which is 14.7 cal. less than the av. for full-time infants (Benedict and Talbot). The group included infants from 3 days to 3 months of age; 6 of the 22 were studied during the first 11 days of life and the metabolism was less than 400 cal.

C. V. B.

**Increased blood sugar coincident with ovulation in pigeons.** H. E. HONEYWELL AND O. RIDDLE. *Proc. Soc. Exptl. Biol. Med.* 19, 377-80(1922).—Blood samples were obtained by puncture of the heart and analyzed by the method of McLean. Coincident with ovulation there occurred an increase of the sugar of the blood to 25% or more above the preovulation value.

C. V. B.

**A comparison of the alkaline tide in urine with the results of fractional gastric analysis.** R. S. HUBBARD AND S. A. MUNFORD. *Proc. Soc. Exptl. Biol. Med.* 19, 429-30(1922).—The alkaline tide was present in patients with free HCl in the gastric contents, and absent in cases of anacidity.

C. V. B.

**The blood chemistry of thyroidectomized sheep.** A. BODANSKY. *Proc. Soc. Exptl. Biol. Med.* 19, 430-1(1922).—Blood drawn in the morning before feeding was analyzed by the procedure of Folin and Wu. Sugar ranged from 0.06 to 0.07% in normal animals and from 0.04 to 0.05% in the thyroidectomized. The values for non-protein N were for normal sheep 40-42 mg., for thyroidectomized sheep 28-32 mg. per 100 cc. of blood. Blood drawn several hrs. after the morning meal gave for sugar 0.1-0.12% in controls, 0.06-0.07% in the thyroidectomized.

C. V. B.

**Basal metabolism of premature and undersized infants.** J. R. MURLIN AND E. MARSH. *Proc. Soc. Exptl. Biol. Med.* 19, 431-3(1922).—Tests were made during sleep in the respiration incubator (Murlin) at a temp. of 27°. Ten newborn infants, all under 5 lbs. 5 oz. at birth, were studied. The av. basal heat production was 24.63 cal. per sq. m. (Lissauer) per hr. Four infants subsequently died, the av. of the remaining 6 was 25.8 cal. per sq. m. per hr. Six normal infants born at term had a heat production

of 27.3 cal. per sq. m. per hr. (Lissauer). The test will be of value as a means of prognosis in prematurity. C. V. B.

**The relative lipid-content of plasma and serum.** PAULETTE JUNG AND R. WOLFF. *Bull. soc. chim. biol.* 5, 137-47 (1923).—Spontaneous coagulation of dog blood is almost always accompanied by increase of fats, cholesterol, and phospholipoids in the liquid portion. Serum is richer than plasma in lipoids. The increase varies according to the nutritive condition of the animal—when fasting the difference is slight. After a meat meal serum shows, compared with plasma, a more marked increase of P than of fatty acid, suggesting increase of non-phosphatide. After a meal of butter or carbohydrate fatty acids especially are increased in the serum. A. T. CAMERON

**The role of catalase in the respiration of embryos.** K. BIALASZEWICZ. *Trav. lab. physiol. Inst. M. Nencki* 1, No. 8, 12; *Chem. Zentr.* 1922, III, 279.—Contrary to the opinion of Loews no relation was found between the intensity of respiration and the amt. of catalase in the frog embryo, though the sensitiveness of the cell plasma toward  $H_2O_2$  increased with the rate of respiration. C. C. DAVIS

**Relations between the size of the heart and the composition of the blood.** ERICH MEYER AND RICHARD SEYDERHELM. *Ver. deut. Ges. inn. Med.* 1921, 376-8; *Chem. Zentr.* 1922, III, 295.—Through venesection of 30 or 40 cc. a contraction of the heart of dogs occurred with return to normal size in 24-36 hrs. This contraction was greatest when the serum concn. had reached its lowest point. Injection of physiol. NaCl solns. after the venesection did not decrease the time required for a return to normal size, but solns. of gum arabic did have this effect. Repeated small venesections brought about enlargement of the heart. C. C. DAVIS

**Albumoses in the blood.** FELIX KLENITZ. *Ver. deut. Ges. inn. Med.* 1921, 416-21; *Chem. Zentr.* 1922, III, 297.—The presence of non-coagulable protein decomposition products which form biuret is not characteristic of fever or any particular disease and is found in normal human and animal blood. C. C. DAVIS

**The relation between glycogen content and the reaction of the vaginal secretion in human beings and certain domestic animals.** C. PASCH. *Zentr. Gynakol.* 46, 375-7; *Chem. Zentr.* 1922, III, 305.—Unlike that of women, the vaginal secretions of guinea pigs, rabbits and cows gave an alk. reaction. This is related to the lack of glycogen in the mucous membrane epithelia in these animals. C. C. DAVIS

**A few principles of metabolism.** M. v. GRUBER. *Sitz. Bayr. Akad. Wiss.* 1921, 341-54; *Chem. Zentr.* 1922, III, 565.—The production of heat in a person, his total consumption of potential energy in a unit time, is inversely proportional to his av. cross sectional area and directly proportional to the length of his body. The consumption of energy per unit body length is the same for children and for adults. Directly after puberty the value is somewhat greater. C. C. DAVIS

**Investigations on the tryptophan content in human milk and that of some animals with special reference to the age of the milk.** COSTANZA BOCCADORO. *Pediatrica* 30, 257-78; *Chem. Zentr.* 1922, III, 585.—Tryptophan detd. according to Fürth and Nobel was for women at the beginning of lactation 11% of the total protein, decreasing to 7.4-4.8% during the following months. In the cow it was 9.3-14.1%, the goat 8.6-9.4%, the mare 9.3-10.1% of the total protein. C. C. DAVIS

**The problem of hormones in muscular tissue.** S. A. KOMAROFF. *Wratschebnaja delo* 1921, 1-6, 11-5; *Chem. Zentr.* 1922, III, 630-7.—Carnosine acts as a powerful stimulant to intestinal secretions and to the motor functions of the intestines. Histidine and carnitine act in a similar manner but less powerfully. Methylguanidine stimulates the secretion of the stomach, salivary glands, the pancreas, liver and other glands. Probably all extractives of the muscular tissue enter the blood and act as hormones. C. C. DAVIS

**The action of bile substances on the nerves.** J. I. PERICHANJANZ. *Wratschebnaja delo* No. 22-4 (1921); *Chem. Zentr.* 1922, III, 637.—Dil. solns. of bile (1:9) at first greatly increase the irritability, concd. solns. (1:5) slightly. C. C. DAVIS

**The role of the liver in protein metabolism.** NOEL FIESSINGER AND RENE CLOGNE. *J. med. franc.* 11, 64-71; *Chem. Zentr.* 1922, III, 1069.—A review of the functions of the liver in health and in certain diseases. C. C. DAVIS

**The water content of human erythrocytes and its determination.** ROBERT STEINBACH. *Z. Biologie* 75, 305-8; *Chem. Zentr.* 1922, III, 1240.—A detn. of the  $H_2O$  content of the total dry substance of venous blood and that of the dry substance of the serum by means of the micro method (tortion balance) gave values of 57.5 and 57.3% for men and women, resp. C. C. DAVIS

**The origin, life and amount of blood sugar.** E. J. LESSER. *Naturwissenschaften* 11, 422-5 (1923).—A resume. C. C. DAVIS

**The regulation of respiration and reaction.** HANS WINTERSTEIN. *Naturwissenschaften* 11, 625-30, 644-51(1923).—A review and discussion with a bibliography.

C. C. DAVIS

**The study of the physiology of the thyroid in frogs.** T. GAYDA. *Arch. sci. biol.* 3, 415-23(1922); *Physiol. Abstracts* 7, 371.—Thyroid feeding, thyroid grafting, and thyroidectomy have almost no effect on the production of heat in adult frogs.

JOSEPH S. HEPBURN

**Heat production in depancreatized frogs and in frogs deprived of the suprarenal capsule.** T. GAYDA. *Giorn. accad. med. Torino* 24, 401-7(1922); *Physiol. Abstracts* 7, 371.—Heat production in frogs is not influenced by removal of the pancreas, but is decreased to 30% of its normal value by partial removal of the adrenals. Should the remnants of the adrenals become necrotic, a further decrease in heat production occurs on the day preceding death.

JOSEPH S. HEPBURN

**The fatty acids of blood plasma.** W. R. BLOOR. *J. Biol. Chem.* 56, 711-24(1923).—"The amts. of total lipid, fatty acid, and unsapon. matter in blood plasma are variable in different species and to a less extent in individuals of the same species, but there is a remarkable constancy in the relationships between the fatty acids and the unsapon. matter (mainly cholesterol) and between the solid (satt.) and liquid (unsatt.) fatty acids which holds for both individuals and species. The unsapon. matter is about  $\frac{1}{2}$  of the total lipid and the liquid fatty acid is about  $\frac{1}{2}$  of the total fatty acids in all. The fatty acid mixt. apparently consists of the same or nearly the same constituents in all samples, as shown by the closely similar m. ps. of the mixts. and of the solid constituent and the similar I numbers of the liquid fraction. The evidence indicates that, in agreement with earlier work, the fatty acids of fasting blood plasma are present in definite compds. which exist in a definitely balanced relation to each other and also that the compn. of the compds. with respect to satt. and unsatt. fatty acids is quite const. through the range of species (sheep, cow, pig, and dog) examd. and over a considerable range of total lipid values." The presence of highly unsatt. fatty acids in the blood as found in the present work was to be expected if Leathes' hypothesis is correct that desatn. is a necessary preliminary step in the utilization of the comparatively stable fatty acids of the food or body stores. The following av. amts. of the substances named, expressed in g. per 1,000 cc., were found in pig (13 samples), beef (16), sheep (18), and dog (6) plasma, resp.: fatty acids, 1.84, 1.54, 1.40, 3.07; unsapon. matter, 1.06, 1.14, 0.78, 1.60; solid fatty acids, 0.53, 0.34, 0.36, 0.68; liquid fatty acids, 1.09, 0.98, 0.88, 1.88. The I numbers of the liquid fatty acids were as follows, resp.: 133, 147, 118, 155.

A. P. LOTHROP

**Studies of the carbon dioxide absorption curve of human blood. III. A further discussion of the form of the absorption curve plotted logarithmically, with a convenient type of interpolation chart.** J. P. PETERS. *J. Biol. Chem.* 56, 745-50(1923); cf. *C. A.* 17, 2133.—The comparison of the two methods of drawing curves previously described has been extended to other available data and in all instances the approx. straight-line curve obtained by plotting  $\log [H_2CO_3]$  against  $\log [BHCO_3]$  has been found to agree with observed data better than does the  $p_H$ - $[BHCO_3]$  relation; this is especially true at low  $CO_2$  tensions. A chart is given, constructed for use with plasma at 38° by assuming a  $p_K$  value of 6.14 and a soly. coeff. at 38° of  $\alpha_{CO_2, \text{ plasma}} = 97.5 \times 0.555$ , which permits a rapid visualization and calcn. of changes in the 3 variables; given values for any two of the 3 functions,  $p_H$ ,  $CO_2$  content, and  $CO_2$  tension of plasma, the third is detd.

A. P. LOTHROP

**Studies of gas and electrolyte equilibria in the blood. V. Factors controlling the electrolyte and water distribution in the blood.** D. D. VAN SLYKE, HSIEN WU AND F. C. McLEAN. *J. Biol. Chem.* 56, 765-849(1923); cf. *C. A.* 16, 3918; 17, 133.—"The present paper is devoted to the quant. formulation and exptl. trial of a physicochem. explanation for the distribution of electrolytes and  $H_2O$  between cells and plasma, and of the influence on the distribution of such factors as addn. or loss of  $CO_2$ ,  $O_2$ , acids, alkali, and salt. On the basis of the assumption that the laws holding in dil. solns. for (1) the relationships between the reaction and the amts. of base bound by weak and strong acids, (2) the distribution of diffusible and non-diffusible electrolytes on two sides of a membrane (Donnan), and (3) the proportionality between the ratio mols. + ions of solute/mols. of  $H_2O$  and the osmotic pressure, are also valid for blood, mathematical expressions have been derived which predict the distribution of electrolytes and  $H_2O$  between cells and serum, and the manner in which the distribution is affected by changes in  $p_H$  and  $O_2$  content. The effects of varying  $CO_2$  tensions have been investigated and the results have been found to approximate those predicted. Calcs. based on the data of Loeb, Atchley, and Palmer (*C. A.* 16, 2550) indicate the probability that the same

physicochem. laws defined for the cells-serum equil. govern the distribution of electrolytes between blood serum and fluids in the serous cavities, although the permeabilities of the  $\text{O}_2$  membranes are different and conditions are such that exact osmotic equality cannot apparently exist between the serum and fluids. Applied to the methods for detg. blood  $p_H$  by the  $\text{CO}_2$  capacity and dialysis methods, the data obtained have been used to est. the corrections necessary because of the heterogeneous character of the blood in the former case and the Donnan membrane effect in the latter. In addn. to supplying evidence concerning the validity of the theoretical considerations advanced in this paper, the exptl. data demonstrate the following: The base bound by the cell proteins of oxygenated horse blood over the physiol.  $p_H$  range is approx. expressed in milliequivalents by the equation  $[BP]_e = 3.6[Hb]_e$  ( $p_{H,e} \rightarrow 0.6$ ), when  $Hb$  expresses millimols of hemoglobin in terms of  $\text{O}_2$  capacity. The  $[BP]_e$ ,  $p_{H,e}$  curve is slightly concave towards the  $p_H$  ordinate, so that the above linear equation is an approx. expression of the results. The base bound by the serum proteins is indicated, over the physiol. range of reaction, by the equation  $BP_s = 0.008 P_s$  ( $p_{H,s} \rightarrow 4.80$ ), where  $P_s$  expresses g. of serum protein. The osmolar concns. in blood cells and serum are equal when calcd. as mols. + ions of solutes/mols. of  $\text{H}_2\text{O}$ , the electrolytes being assumed to be equally dissociated in cells and serum."

A. P. LOTHROP

The ultra-violet absorption spectra of cerebrospinal fluid. T. SHIONOVA. *J. Tokyo Med. Soc.* 36, No. 11(1922); *Japan Med. World* 3, 78(1923).—S. tested the cerebrospinal fluid by means of an elec. arc from iron electrodes. There is a quant. absorption of the ultra-violet rays by the protein of the spinal fluid. M. E. MAVER

The amylase of saliva and pancreatic juice. K. GYOTOKU AND J. OHHASHI. *Med. News (Japan)* No. 1109 (1923); *Japan Med. World* 3, 107.—Using a definite phosphate buffer soln. the authors found the optimum temp. for the amylase action of both saliva and pancreatic juice to be 53–55°, without a marked decrease in activity at 60°.

M. E. MAVER

Normal Japanese urine. K. TAKAHASHI. *J. Tokyo Med. Soc.* 37, No. 1(1923); *Japan Med. World* 3, 138.—The urine of 100 soldiers and 200 laborers was examd. The av. quantity for 24 hrs. was 1459 cc., the max. was 3100 cc., and the min. 430 cc. The av. sp. gr. was 1017, the max. being 1033 and the min. 1007. The av. quantity of N per kg. body wt. was 0.156 g., varying from 0.03 to 0.33 g. Reducing substances corresponding to an av. of 0.165% glucose were found.

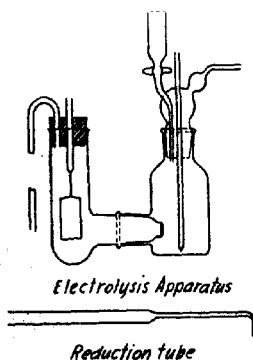
M. E. MAVER

Investigations on the blood sugar in man. Conditions of oscillations, rise and distribution. K. M. HANSEN. *Acta Med. Scand., Suppl. IV* 1923, 224 pp.—With the aid of a well calibrated micromethod blood sugar detns. were made at very frequent intervals, on 0.1 cc. of blood from the ear for each analysis. The fasting blood sugar in the same individual and on the same day is not an absolutely const. quantity, but oscillates up and down. In normal persons it varies within the limits of 0.08–0.11%; it is seldom higher than 0.11 or lower than 0.07%. This is equally true for capillary and vein blood. The oscillations in the blood sugar content are found likewise in fasting diabetics. Similarly, after ingestion of carbohydrate the blood sugar rises, not however as a smoothly running curve but with wave formation at the surface of the main rise. These superimposed waves are particularly large and frequent where the curve has reached the highest level and forms a plateau, prior to the beginning of its decline. Since these waves have been observed 3–36 hrs. after a meal it is assumed that they represent a const. and regular occurrence, and are supposed to be associated with processes of blood sugar regulation. When glucose is administered there is a definite upper limit for the rise in the blood sugar level which in normal persons rarely exceeds 0.18%. The existence of this upper limit regardless of the amt. administered is thought to be due to the phenomenon of acceleration of the removal of sugar from the blood stream, an acceleration which reaches its greatest capacity at that concn. This increased acceleration may possibly be the result of an increased supply of pancreatic hormone. In diabetes with repeated doses of glucose a difference in the blood sugar level is observed which is proportional to the increase in the size of the dose; the total curve is, therefore, a straight line. In mild cases some power of acceleration of the removal of glucose from the blood stream may be retained though at a hypernormal blood sugar concn. The rise in blood sugar level for a definite period is the same per g. of glucose administered, but this may be quant. reduced when through any means the organism's condition has improved. An excessive diet generally leads to an increase in the 1-g. rise. This fundamental fact is made the basis of a proposed functional test for diabetes. It is proposed to employ the numerical value of the one-g. rise measured by glucose administration during the aglucosuric period as a general measure of the diabetic condition. A detn. of the acceleration power by means of glucose administration and con-

struction of the total curve is also proposed as a functional test for carbohydrate metabolism in the unclassified glucosurias. The dose of glucose administered, however, must be large as the acceleration power has an optimum blood sugar concentration higher than normal, and the results obtained with small doses may be very ambiguous. In 93% of the normal individuals examined the sugar percentage in the plasma and in the corpuscles was the same. After glucose administration in normal persons as well as in diabetics an equalization of the plasma and cell sugar seems to take place rapidly though not instantaneously.

S. MORGULIS

**Arsenic in blood and in cerebrospinal fluid.** LEONARD BRAHME. *Acta Med. Scand., Suppl. V* 1923, 240 pp.—Arsenic may be found as a component of various organs even when no As is being purposely administered. This is likewise true for the urine. The source of the As in these circumstances is the food, since As is present in sea-water and in the soil and thus gains access to both the vegetable and animal products which constitute the human diet. In actual poisoning with As preps, the substance is unevenly distributed in the different organs of the body but there is no evidence of its selective accumulation in the liver. In the therapeutic treatment with As preps, it is not possible to judge the retention of the substance by the urinary findings, inasmuch as the largest amt. of it may be eliminated through the intestines or some other way. The problem of estg. the As content of the blood and cerebrospinal fluid encounters the greatest difficulty in the fact (1) that only small quantities of material are available for analysis and (2) that the As amts. may vary from 1 mg. to 0.001 mg. *Method of analysis.*—B. utilizes the principle of Ramberg and Sjöström by which As in quantities of 0.0002–5.0 mg. can be detd. with an accuracy of  $\pm 0.00001$  mg. The method does not depend on the use of As-free reagents; the reagents are the purest that can be obtained, and a correction is made from a blank detn. Under properly controlled conditions this correction was only 0.0003–0.0006 mg. As. To 8–12 cc. of blood or cerebrospinal fluid in a 100-cc. Kjeldahl flask provided with a condenser tube having a ground joint add 5 cc.  $H_2SO_4$  and 2 cc.  $HNO_3$  and very carefully digest to destroy the org. matter. When this has been completed, as can be recognized by the fact that the soln. becomes clear, continue the boiling for another  $\frac{1}{2}$  hr., cool, and add 7 cc. of satd.  $(NH_4)_2C_2O_4$  to remove the nitroso compds. Should there be no evolution of gas at this stage it would indicate that the org. matter was not completely digested, and the boiling with acid must be resumed. When through the treatment with  $(NH_4)_2C_2O_4$  all the formed oxides of N have been removed, cool the contents of the flask and dil. with 5 cc.  $H_2O$ . Cool once more and treat with 0.2 g.  $N_2H_4 \cdot H_2SO_4$ , 6 g. KCl and 10 cc. HCl. (The KCl may be omitted and 15 cc. HCl used instead); also add a few grains of KBr. Distil for 5 min. with a flame adjusted so as to start the boiling in 45 sec. Slightly warm the distillate and titrate with  $KBrO_3$  soln. (contg. 0.1485 g.  $KBrO_3$  per l., 1 cc. of which corresponds to 0.2 mg. As) using methyl orange as indicator. This titration is impossible except with an absolutely Cl-free HCl. The end point is the disappearance of the Me orange color. A correction must be made in the titration for the amt. of  $KBrO_3$  taken up by the water. When, however, the amt. of As is too small to be detected titrimetrically, the distillate must be worked over again and the As detd. by a different procedure. This modified process was frequently needed as in most analyses the quantity of As did not exceed 0.008 mg. Transfer the distillate to a porcelain evapg. dish together with 2 cc.  $HNO_3$  and evap. to dryness on the water bath. Add 5 cc. 10%  $H_2SO_4$  and evap. to a small vol. The  $HNO_3$  must be completely gotten rid of. Transfer quant. to an electrolysis app. (see fig.). The app. is all made of glass and consists of 2 chambers: a large cathode, and small anode chamber, separated by a semipermeable membrane. Enough Hg is poured into the first to cover the bottom; then both chambers are filled with 10%  $H_2SO_4$ . A bent tube passes through the stopper



of the anode chamber and dips several cm. into the water which surrounds the app. The gas produced in the electrolysis passes out of this tube and the extra resistance offered by the water serves to counteract the tendency of the fluid to flow from the cathode to the anode chamber. Both Pt electrodes are fused to glass tubes which

are filled with Hg. A 3 amp. current at about 125 v. is required. The glass top of the cathode chamber is provided with a side tube to which is connected by means of rubber tubing a 12 cm. long piece of Jena glass tube, 1 cm. in diam. This tube must be of sufficient hardness to withstand the heating during the reduction process. Having ascertained that the entire app. is free from air, heat the reduction tube until it begins to glow, and pour the soln. in the porcelain dish into the cathode chamber through the funnel. Electrolyze for 30 min. The  $AsH_3$  produced is decomposed by the heat and the As is deposited in the capillary part of the reduction tube. Cut the capillary part of the tube contg. the As mirror into a number of pieces and place in a glass-stoppered tube of about 3-cc. capacity. Fill this with 2 cc. of a 0.0005 N  $I_2$  soln., wrap in black paper and shake mechanically until the As mirror is completely dissolved. Wash into a small beaker and titrate the excess  $I_2$  with 0.0005 N arsenic acid. Less than 0.0001 mg. As can be detd. *Experiments on blood.*—Under certain dietetic conditions there is sufficient As in the blood that it can be detd. even in small vols. The exptl. evidence seems to point to fish as the principal As-contg. food. It is important to note that even under physiological conditions As may be present in the blood. When a 0.5% Liquor Arsenit. Kalie. is administered the As content of the blood reaches a max. after several days (6-10). This max. level is then retained for a few days before the As content commences to diminish very gradually (to 58% of the max. value in 56 days). When the Liquor Arsenit. Kalie. is being repeatedly administered a max. blood content is likewise established after a while, but although the amt. of As taken in from day to day remains the same the concn. in the blood commences to diminish. The flat part of the curve (the plateau) of the blood As corresponds to a concn. of 0.0012-0.0020 mg. per 10 cc. blood at which concn. a balance is apparently established between the absorption and excretion. The ensuing fall in the concn. of As in spite of a uniform administration is attributed to an acquired immunity of the intestine towards the substance, which it no longer absorbs with the same efficiency. When As is given in the form of nearsphenamine the As content of the blood diminishes very rapidly in the first few hrs. following the injection because the substance is deposited in parenchymatous organs, and probably also in the mucous membranes and in the skin epithelium. Already 12 hrs. after an injection the amt. of As circulating in the blood is a very small fraction of the injected quantity. The As concn. of the blood is not only more or less proportional to the dose of nearsphenamine, but even with similar doses it tends to increase with the number of injections. When 0.15 g. nearsphenamine was given no As could be found in the blood 24 hrs. later. With doses 0.3-0.45 g. each the As in the blood could occasionally be detected 48-96 hrs. later. When 0.6 g. was injected, As was found in blood up to 120 hrs., after repeating the dose up to 168 hrs., and after the 3rd. 5th dose even up to 216 hrs. In all these instances, however, the amt. of As per 10 cc. blood was less than 0.001 mg. *Experiments on cerebrospinal fluid.*—Administration of As by mouth in the form of Liquor Arsenit. Kalie. (daily dose equal to 7.5 mg. arsenic acid) has led to the detection of As in the cerebrospinal fluid of only those persons who exhibited symptoms of meningeal irritation. Following injections of nearsphenamine no As could be demonstrated in the cerebrospinal fluid except in cases where there was evidence of meningeal irritation (judged by the cell count). But even in those persons who showed a great concn. of As in the cerebrospinal fluid the quantity of As did not exceed a few thousandths of a mg. per 10 cc. The As could be detected 5-10 min. after an injection of nearsphenamine. It is probable that As disappears from the cerebrospinal fluid within 24 hrs. With nearsphenamine the As concn. in the cerebrospinal fluid never exceeded  $\frac{1}{4}$  that of the blood, which is considerably lower than was found with the administration of Liquor Arsenit. Kalie. by mouth. S. MOROZULIS.

**Extractive substances in the skeletal muscles of man.** I. A. SMORODINTZEV. *J. Russ. Phys. Chem. Soc.* 49, 1, 263-6(1917).—The extractives were prepd. from the muscles of a freshly amputated leg. The methods employed were previously described (*Bull. Acad. Sci. Russie* 1916, 1535). The following table is given, as % of fresh tissue: total extractive N 0.45, purine substances 0.036, carnosine 0.164, methylguanidine 0.011, carnitine 0.031, creatinine present. W. A. PERLZWEIG.

**Source of Indian yellow.** WILHELM WIECHOWSKI. *Arch. exptl. Path. Pharmacol.* 97, 462-88(1923).—Feeding expts. with rabbits indicate that mangin is the source of both euxanthic acid and Indian yellow. G. H. S.

**Metabolic physiology of the surviving mammalian heart.** I. FELIX KLEWITZ. *Arch. exptl. Path. Pharmacol.* 98, 91-105(1923).—With the mammalian heart not only do dextrose and glycogen serve as sources of energy, but most probably the fats and certainly N-contg. substances, at least occasionally, are drawn upon for energy. This is the case in normal animals, although it may be the exception, as it is in animals which

have been deprived of glycogen by starvation or by phlorhizin treatment. Creatine and creatinine are eliminated by the heart in variable amts. G. H. S.

## G—PATHOLOGY

H. GIDEON WELLS

The existence of different immunological types of *B. pertussis*. C. KRUMWIEDE AND L. MISHULOW. *Proc. Soc. Exptl. Biol. Med.* 19, 201(1922).—Agglutination and agglutinin absorption reactions divide strains of *B. pertussis* into 2 serological groups; antiserums for group "b" agglutinate the strains of group "b" and slightly or not at all those of group "a." The absorption of "b" serum by "a" strains does not reduce "b" agglutinins. Group "a" serum agglutinates "b" strains; the absorption of "a" serum by "b" strains reduces the agglutinins for "a." The findings have a possible bearing on the use of pertussis vaccines. C. V. BAILEY

Further studies on ligation of the thyroid arteries in depancreatized diabetic dogs. II. The relation of the thyroid and parathyroids to pancreatic diabetes in dogs. G. A. FRIEDMAN AND J. GOTTESMAN. *Proc. Soc. Exptl. Biol. Med.* 19, 209-21(1922).—Complete ligation of the thyroid arteries or thyroidectomy in depancreatized dogs diminished the sugar of the blood and checked glucosuria. Glucosuria persisted if tetany or infection developed. Partial ligation increased the sugar in the blood. Tetany, following partial parathyroidectomy and thyroidectomy, is more apt to occur in diabetic than in normal dogs. Intravenous injections of Ca lactate temporarily prevented the seizures. C. V. B.

The amount and distribution of stainable lipid material in renal epithelium in normal and acutely nephropathic animals, with observations on the functional response of the kidney. W. D. MACNIDER. *Proc. Soc. Exptl. Biol. Med.* 19, 222-7(1922).—Dogs were rendered acutely nephropathic by 1 subcutaneous injection of 6 mg. of uranium nitrate per kg. and the kidneys examd. at intervals of 6, 12, 24 and 48 hrs. later. Frozen sections were stained for lipid material by Herxheimer's Scharlach R method. Lipid material was constantly found in the cells of the loop of Henle in normal dogs. Uranium first caused an increase of lipid in the cells of the loop without functional changes; after 12 hrs. kidney function was impaired and lipid was found in the cells of the convoluted tubules. C. V. B.

The bicarbonate and chloride content of the blood in certain cases of persistent vomiting. H. A. MURRAY, JR. *Proc. Soc. Exptl. Biol. Med.* 19, 273-5(1922).—The 7 patients examd. had obstruction at or near the pylorus with inordinate vomiting 4 days to 2 months in duration. The  $\text{CO}_2$  tension of the blood varied from 70 to 107 vols.  $\%$ ; it was highest in cases with tetany. The chloride content of the blood was lowered (4.5-2.2 g. per l.). The Na remained unchanged. The results are explained by loss of HCl in the vomitus. The  $p_{\text{H}}$  of the blood remained unchanged until just before death. Different samples of blood were used for the  $p_{\text{H}}$  and  $\text{CO}_2$  tension estns. C. V. B.

Some problems of diabetes mellitus. L. B. WINTER AND W. SMITH. *Brit. Med. J.* 1923, I, 711-5; cf. *C. A.* 17, 1502.—Normal blood sugar of man and animals has a lower rotatory power than  $\alpha,\beta$ -glucose, and is probably of a reactive nature. Blood sugar of diabetics is mainly  $\alpha,\beta$ -glucose. A more complex sugar is also present in diabetic blood. Injection of insulin causes a change in the nature of the blood sugar, the complex sugar disappearing. Insulin and liver ext. together alter the rotatory powers of  $\alpha,\beta$ -glucose *in vitro*. Injection of adrenaline into normal rabbits causes the blood sugar to alter towards the condition in diabetics. Ext. of yeast, tested on animals and human diabetics, has an effect similar to that of insulin. A. T. CAMERON

Nature of blood sugar. J. A. HEWITT. *Brit. Med. J.* 1923, I, 994-5.—Criticism of previous paper. W. SMITH AND L. B. WINTER. *Brit. Med. J.* 1923, I, 1039. Reply. A. T. CAMERON

Composition of the gases in artificial pneumothorax. L. HILL AND J. A. CAMPBELL. *Brit. Med. J.* 1923, I, 752-4.—The  $\%$  of  $\text{CO}_2$  in gases of the pneumothorax appears to approximate rapidly to that of the blood bathing the compressed lung. The  $\%$  of O approximates slowly to that in the tissues bounding the cavity. Pathological fluids and tissues usually cause abnormally high percents of  $\text{CO}_2$  and probably lower O content. A. T. CAMERON

Value of laboratory tests in diseases of the liver and pancreas. W. L. BROWN. *Brit. Med. J.* 1923, I, 461-1.—A general treatment. A. T. CAMERON

Adrenaline as a potential factor in hyperthyroidism. D. J. HARRIES. *Brit. Med. J.* 1923, I, 1015-6.—It is suggested that bacterial action in the intestine may produce

adrenaline precursors other than tyrosine, and that cessation of putrefactive action may lead to diminution of adrenaline production!

A. T. CAMERON

**Behavior of the blood sugar under the action of insulin and other agents.** G. S. EADIE. *Brit. Med. J.* 1923, II, 60-1.—Repetition of Winter and Smith's work gave solns. with different rotating and reducing power values. (In an added note J. J. R. Macleod concludes that it would be rash at present to consider that  $\gamma$ -glucose is necessarily responsible and suggests that the complicated chem. procedure necessary to prep. the soln. for the polariscope may be responsible for the production of substances with a lower rotating power.)

A. T. CAMERON

**Variation in the lipid content of blood plasma after injection of peptone. Comparison with anaphylactic shock.** PAULETTE JUNG AND R. WOLFF. *Bull. soc. chim. biol.* 5, 200-6(1923).—After intravenous injection of peptone lipid equib. of the blood plasma is profoundly modified: the total fatty acid content is considerably augmented. Equib. tends to reestablish itself when the plasma is again coagulable. Anaphylactic shock produces a modification of lipid content in the plasma.

A. T. CAMERON

**Placental iron and its relationship to icterus neonatorum.** A. C. WILLIAMSON. *Surgery, Gynecology, Obstetrics* 37, 57-62(1923).—All new-born infants have bilirubinemia corresponding to the Fe content of the placenta. There is a definite relationship between icterus neonatorum and placental Fe content. The greater the latter the greater the clinical jaundice, which may thus be considered as of purely dynamic or hemolytic in origin. Non-icteric infants have a certain degree of bilirubinemia but no jaundice since their placental Fe content is below the necessary level.

A. T. CAMERON

**Contribution to the study of the hemolysins and agglutinins.** JAN LUKES AND KAREL BULOHRADSKY. *Biok. listy* 8, 45-8(1921); *Chem. Zentr.* 1922, III, 749. The hemolytic and agglutinating action of serum was not reduced after coagulation with EtOH and Me<sub>2</sub>CO (extn. of lipids) insofar as denaturing was concerned, but depended on the soly. of the albumins. No trace of hemolysins or agglutinins could be detected in the ext.

C. C. DAVIS

**The quantity and quality of cerebral lipids in the brain of dogs with rabies.** GIOVANNI BATTISTA FACCHINI. *Bull. science med.* 10, 82-90; *Chem. Zentr.* 1922, III, 1009. —The content of total lipids in the brain of a dog with rabies averaged somewhat less than was found by Novi in healthy dogs. Phosphatides were distinctly less while the sum of cholesterol plus fat was higher.

C. C. DAVIS

**Contribution to the study of lime metabolism in diabetes.** F. CALDI AND G. E. PUXEDDU. *Folia med.* 8, 68-77, 109-20; *Chem. Zentr.* 1922, III, 566.—The Ca retention after administration of Ca lactate was less for diabetic patients than for healthy persons, whereas the Ca content increased. The excretion of Ca varied from the normal insofar as the greater part was eliminated in the urine and only a small part in the feces.

C. C. DAVIS

**Studies of alimentary glucosuria.** J. E. HOLST. *Ugeskrift Læger* 84, 224-34; *Chem. Zentr.* 1922, III, 736; cf. *C. A.* 17, 2317.—A report of studies of 14 healthy persons and 145 patients with various diseases but without any trace of diabetes after a diet rich in carbohydrates. Alimentary glucosuria appearing in a number of cases is explained as a symptom of a disturbance of carbohydrate metabolism.

C. C. DAVIS

**Cholesterol metabolism.** GROSS. *Ver. deut. ges. inn. Med.* 1921, 343-9; *Chem. Zentr.* 1922, IV, 220.—Cholesterol is not excreted in the urine even after the administration of large amts. In all cases of nephropathy, with the exception of amyloid kidney, cholesteroluria is, however, present. In nephrosis, cholesterol can be detected microscopically as an isotropic substance and in glomerulus nephritis chemically in the urine. With a lipid-poor, fat-free diet, the amt. of cholesterol decreases in the blood and urine and increases again on a mixed diet. Therefore at least a greater part of the cholesterol in the blood depends upon diet. The fact that amyloid kidneys do not excrete cholesterol can be utilized in diagnosis.

C. C. DAVIS

**Standard technic for the Widal reaction.** C. R. MADDEN. *Abstracts Bact.* 5, 13 (1921).—Sufficient blood to yield 1 cc. of serum is drawn into a sterile tube or Kiedle vacuum bulb; the serum is obtained by centrifugation or clotting. Bacterial suspensions are obtained from freshly grown agar slants, preferably 18 hrs. and not over 24 hrs. old, by emulsification in saline soln. The serum, bacterial suspension, and saline soln. are mixed in sterile, chem. clean serological tubes. Each tube receives 0.1 cc. of the bacterial suspension, and the total vol. of each reacting mixt. is 1.0 cc. The saline and serum are used in such amts. that 4 tubes contain serum at a total diln. of 1:10, 1:20, 1:50 and 1:100, while a fifth tube is a control without serum. Three sets of tubes are prepd. with *B. typhosus*, *B. paratyphosus* A, and *B. paratyphosus* B, resp. The tubes are kept in an incubator for 1 hr., readings for agglutination being made every



15 min., then are kept in an ice box for 12 hrs. with readings every 2 hrs.

JOSEPH S. HEPBURN

**Rate of destruction of the so-called syphilitic antibodies by heat.** R. L. KAHN AND A. G. BOYD. *Abstracts Bact.* 5, 17(1921).—Use was made of an alc. antigen from beef heart and a cholesterolized antigen from pig heart. When fixation occurred at incubator temp. for 30 min., strongly positive sera showed a loss of approx. 5% of their antibodies during the preliminary heating at 56° for periods as long as 60 min., weakly positive sera a loss of as much as 50% of their antibodies during preliminary heating at this temp. for 30 min. Frequently the antibodies were entirely destroyed by a temp. of 62°. When fixation occurred in an ice box for 4 hrs., most sera tended to be somewhat stronger rather than weaker after the preliminary heating, a few weakly positive sera showed approx. 75% increase in antibodies after the preliminary heating.

JOSEPH S. HEPBURN

**Effect of inactivation on the antibody content of syphilitic sera.** R. L. KAHN AND A. G. BOYD. *Abstracts Bact.* 5, 24(1921).—The results obtained are essentially the same as those reported in a previous communication. Cf. preceding abstract.

JOSEPH S. HEPBURN

**Horse serum protection against diphtheria inoculation.** HENRIETTA CALHOUN. *Abstracts Bact.* 5, 18(1921).—If a single dose of normal horse serum be given intracardially to a guinea pig at any time from 48 hrs. before to 4 hrs. after subcutaneous administration of a virulent culture of diphtheria bacilli, the animal is protected from death. The antitoxin equiv. of the single dose of normal serum is between 2 and 3 standard antitoxin units; its protective action in this expt. is equal to that given by 6 standard units; the immune factors involved are the antitoxin equiv. of the serum, and its non-specific protein reaction in the guinea pig measured by the leucocyte increase in the blood.

JOSEPH S. HEPBURN

**Effect of bacterial proteins upon intestinal loops of normal and vaccinated animals.** N. P. SHERWOOD AND O. O. STOLAND. *Abstracts Bact.* 5, 18-9(1921).—Intestinal loops from normal guinea pigs and from guinea pigs treated with bacterial vaccines showed approx. the same threshold for stimulation by bacterial proteins, but loops from vaccinated animals responded with a greater intensity. The response, a rise in tone and a temporary decrease in contractions, apparently was nonspecific. Intestinal loops from rabbits were more refractory.

JOSEPH S. HEPBURN

**Testing of antistreptococcic serum.** ELLA M. A. ENLWS. *Abstracts Bact.* 5, 26(1921).—Both the agglutination test and the mouse protection test showed that antistreptococcic serum contained antibodies for only the particular type or types of streptococci which were used as antigens in its production.

JOSEPH S. HEPBURN

**Researches on glucemia and their application to the study of diabetes.** M. LABBÉ. *Bruxelles médical* 2, 251-3(1922); *Physiol. Abstracts* 7, 309.—The dextrose threshold can be detd. only by measurement of the degree of glucemia which corresponds to the appearance of dextrose in, and its disappearance from, the urine. This threshold varies with the individual, the stage of glucosuria and even from day to day in the same person. For detn. of the blood sugar curve after ingestion of dextrose, 50 g. of anhyd. dextrose are given.

JOSEPH S. HEPBURN

**Quantitative relation between complement fixation and agglutination.** PEARL L. KENDRICK AND R. L. KAHN. *Sci. Proc. Soc. Am. Bacteriologists* 1922, *Abstracts Bact.* 7, 25(1923).—"If a series of antityphoid serum dilns. is mixed with a titrated amt. of sp. antigen in duplication and 1 series is observed directly for agglutination while the other is observed for complement fixation, the relative sensitiveness of the 2 reactions appears to depend on the antigen employed.... If a series of syphilitic serum dilns. is mixed with a titrated amt. of ext. antigen also in duplication and comparative tests are made in complement fixation and pptn., the former test is more sensitive than the latter."

JOSEPH S. HEPBURN

**Some influences of hydrogen-ion concentration upon antigenic properties of proteins.** I. S. FALK AND M. F. CAULFIELD. *Sci. Proc. Soc. Am. Bacteriologists* 1922, *Abstracts Bact.* 7, 27(1923).—Anaphylaxis is not produced in guinea pigs by the intravenous or intraperitoneal administration of gelatin soln. at the isoelec. point ( $p_H$  4.7), or more acid, or more alk. Cryst. ovalbumin is more potent when administered to guinea pigs in a soln. more acid than its isoelec. point than at that point ( $p_H$  4.8), or in alk. soln. Sensitization with 5 mg. at  $p_H$  2.0 to 2.5 and intoxication with 50 mg. produce acute anaphylaxis, usually fatal regardless of the  $p_H$  of the intoxicating dose. Sensitization with 5 mg. at a  $p_H$  between 4.7 and 4.8 or between 9.0 and 10.0, regardless of the form of the intoxicating dose, produces anaphylaxis which is practically never fatal. Acute anaphylaxis occurs at any of the 3 H-ion concns. mentioned, if 50 mg.

be used as the sensitizing dose. Similar results are obtained when guinea pigs are passively sensitized by means of serum from rabbits which have been actively sensitized with acid, isoelec. and alk. solns. of ovalbumin. Similar results are also obtained by passive sensitization to cryst. edestin, which is more effective as a sensitizer in acid soln. than at its isoelec. point ( $p_H$  6.9) or in alk. soln.; its intoxicating potency apparently is not influenced by the H-ion concn. at  $p_H$  values between 2 and 10. In the case of ovalbumin, precipitins apparently are produced in the same way as anaphylactic antibodies.

JOSEPH S. HEPBURN.

**Icterus and liver function.** RICHARD BAUER. *Wiener Arch. inn. Med.* 6, 9-26 (1923).—A reliable test for liver function is the hourly estn. of the excretion of galactose in the urine after the administration by mouth of 40 g. galactose. An excretion above 2 g. is considered a positive reaction. Alimentary glucosuria is positive where there is reason to believe the liver cells have been diffusely injured. A severe disturbance of liver function was demonstrated in icterus catarrhalis and hicticus, in subacute and acute atrophy, in fatty infiltration and fatty degeneration in P poisoning and in all forms of cirrhosis of the liver. Inconst., mostly negative findings were obtained in icterus following heart failure, pneumonia, sepsis and infectious diseases. Only negative reactions were found in hemolytic icterus, pernicious anemia and all forms of icterus due to mechanical obstruction.

HARRIET F. HOLMES.

**Permanent arterial high pressure and its relation to kidney insufficiency.** W. FALTA, F. DEPISCH AND F. HÖGLER. *Wiener Arch. inn. Med.* 6, 37-92 (1923). The administration of Na salts leads to a swelling of the colloids of the blood and to an increase in the vol. of the blood. This plethora serosa can be prevented by increasing the blood pressure by the injection of adrenaline. The administration of N, Ca and Mg salts is followed by a shrinking of the blood colloids and a decrease in the vol. of the blood. Increased swelling of the blood colloids is accompanied by decreased diuresis and shrinking of the blood colloids by increased diuresis. The Na salts lead to an increase of blood pressure and the other salts to a decrease of blood pressure. The nonelectrolytes urea and sugar are without effect. The changes in cation relations and water content of the blood brought about by the administration of various salts are of short duration as the regulatory activity of the kidneys soon causes a return to normal relations. In kidney insufficiency there is a functional high blood pressure caused probably by a hyperadrenalinemia as a result of retained metabolic waste products. In later stages the high blood pressure becomes fixed by widespread capillary sclerosis, particularly in the splanchnic region, and at this stage is no longer affected by a NaCl-free diet. The permanent arterial high pressure is a compensatory process hindering the development of hydermia.

HARRIET F. HOLMES.

**Hematoidin and its relation to blood and bile pigment.** G. O. E. LIGNAC. *Arch. path. anat.* (Virchow's) 243, 273-7 (1923).—Hematoidin occurs in tissues in 3 forms, amorphous, cryst., and in soln. staining the tissues. All 3 forms occur in hemorrhages. Cryst. hematoidin is found at the periphery of areas of ischemic necrosis. It occurs in a variety of cryst. forms, particularly as small, anisotropic spheres (globulites) and as anisotropic hair-like needles (trichites). The globulites are usually central and the trichites peripheral and radially arranged in areas of necrosis, the two together resembling a spine-covered sphere. These facts indicate that hematoidin is sol. in tissue juices. A Ca-salt-protein complex occurs in hematoidin globulites. Rhombic columnus and plates of hematoidin are sometimes observed, and are to be considered as mixed crystals, perhaps with Ca salts. Hematoidin belongs to the blood porphyrins or is to be identified with bilirubin. The theory is advanced that hematoidin is formed in areas of ischemic necrosis as a result of oxidation of hemoglobin in which glycogen plays a role.

E. R. LONG.

**The normal urine-sugar curve in normal individuals, borderline diabetics and severe diabetics under insulin treatment.** I. H. PAGE. *J. Lab. Clin. Med.* 8, 631-51 (1923).—The curve of normal sugar excretion hr. by hr. is remarkably const., but with a slight upward trend from morning to evening, with a low level during sleep. The quantity excreted rises for 1 hr. after meals, then sharply falls; the rise is in no way dependent upon the quantity or quality of food ingested. The greatest rise follows breakfast. The curve of normal excretion does not exhibit excursions above 90-110 mg. per hr. Certain borderline diabetics maintain a normal excretion except for a period of 2-4 hrs. per day, 1-2 hrs. after meals. Such glucosurias and those of the severe diabetic can be followed by the hourly observation method, and under insulin treatment the curves may be made to approximate the normal.

E. R. LONG.

**The cause of death in intestinal obstruction.** SETON PRINGLE. *Lancet* 1923, II, 62-4.—The principal factor in causing death in intestinal obstruction is a poison which

is developed chiefly in the duodenum, and although not absorbed from normal intestine is absorbed under the conditions which prevail in obstruction. The compn. of the poison is unknown, but it is almost certainly derived from protein disintegration. The presence of pancreatic secretion, and to a lesser degree the action of bacteria, are probably essential for its production. While the duodenum is the site of max. toxicity in obstruction, yet the poisonous substances are developed lower down in the intestine, and it is probable that in the production of these poisons bacterial action plays a role increasing in importance the lower down the obstruction occurs.

E. R. LONG

**Anaphylaxis studies on the proteins of milk.** F. EISENBERGER. *Z. Immunitäts.* 36, 291-311(1923).—Vigorous physical treatment, as strong heating, does not destroy the anaphylactogenic character of ammoniacal casein soln. Whey protein acts in high degree as a sensitizing and as a shock-causing protein. It does not protect a guinea pig which has been sensitized with ammoniacal casein soln. against casein. Sensitization to ammoniacal casein may be transferred so as to cause passive anaphylaxis. The anaphylactic response in the casein-sensitized animal is highly sp. It is not called forth by heterologous protein, such as other milk protein and various serums. Casein anaphylactic shock exhibits typical symptoms, emphysema, lowered coagulability of the blood, temp. drop, and contraction of bladder and intestinal musculature. Irritation of the sympathetic is seen in the marked dilation of the pupil and constriction of the eye-ground capillaries.

E. R. LONG

**The theory and clinical application of the Meinicke reaction.** II. R. BAUER AND W. NYIRI. *Z. Immunitäts.* 36, 311-20(1923); cf. *C. A.* 16, 2912.—Flocculation in the Meinicke reaction does not depend upon differences in the elec. cond. of ext. and serum. There is no contradiction to the idea of a true immunity reaction, involving lipid antigen and antibody.

E. R. LONG

**Complement as a function of physicochemical factors. Its relation to fever, anaphylaxis, narcosis and intoxication.** HUGO HECHT. *Z. Immunitäts.* 36, 321-37(1923).—Complement function is conditioned by the physicochem., colloidal state of the serum. Into the make-up of this state such factors as surface tension, cond., viscosity and dispersion enter. The complement function occurs only when the colloid particles are of a certain size and electrolytes are present; marked change in particle size or in the electrolytes inactivates it. Activity is restored on restoring former conditions, provided the departure from normal was not great. The change is irreversible if changes in dispersion were great or long continued. Complement function occurs only with combined action of several factors, of which globulin-colloid (middle piece), albumin plus lipid-colloid (end piece) and electrolytes (NaCl and CaCl<sub>2</sub>) are the best known. Change in the physicochem. state of one of these inactivates complement as a whole. A multiple of the protein mol. enters into the smallest unit of the complement function. Such biol. processes as fever, narcosis, anaphylaxis and intoxication, which are accompanied by a change in complement function, are in the end the result of disturbance in the physicochemical balance of the serum.

E. R. LONG

**Investigation of protein and lipid with the aid of saponin hemolysis.** O. EHRENTHEIL AND W. WEIS-OSTBORN. *Z. Immunitäts.* 36, 356-67(1923).—The serum of a pregnant woman has a higher cholesterol concn. than that of a non-pregnant woman and inhibits saponin hemolysis correspondingly. There are occasional divergences from this rule. Shaking an inhibiting serum with ether removes its inhibitory action, while the extd. lipoids restore it. Albumin and globulin alone have no influence on saponin hemolysis, but weaken the inhibitory power of cholesterol. Starch and mastic soln. behave similarly; probably these substances affect the mol. dispersion of the lipid. Very low serum concn. may further saponin hemolysis just as lecithin does. The lecithin content of serum as well as the cholesterol may play some role in saponin hemolysis.

E. R. LONG

**Further results on caroto-central injection of antisera and antigens.** E. FRIEDBERGER AND GERTRUDE MEISSNER. *Z. Immunitäts.* 36, 367-85(1923).—(1) Results with guinea pigs: a rabbit-anti-guinea pig blood serum shows the typical effect of injecting such a serum into the guinea pig blood stream, even when the injection is made into the carotid artery. The serum may be detoxicated by satn. with guinea pig blood, but not by guinea pig kidney. Normal rabbit, beef, eel and pig serums, but not sheep serum, are toxic for the guinea pig on caroto-central injection. Gram-negative bacteria (*B. prodigiosus*, OX 19) cause no immediate symptoms, when introduced by this method, although the animals die in a day or two from foreign protein poisoning. (2) Results with rabbits: Normal pig and beef serum are toxic when injected into the carotid artery, evoking the same symptoms as on intravenous inoculation. (3) Results with mice: Normal pig and beef serums, but not rabbit serum, are toxic

on caroto-central injection. Rabbit-anti-mouse blood serum is typically toxic for mice when injected through the carotid. Anti-sheep corpuscle serum is toxic for mice by the caroto-central route. Satn, with sheep blood does not detoxicate it. It is not detoxicated by mouse brain or liver, but loses its toxicity on satn. with mouse kidney and muscle. This corresponds to the distribution of the sheep hemolysin binding groups in the different organs of this animal species. E. R. LONG.

**Anaphylaxis. LXIV. The behavior of monogenic-polyergic heterogenetic serums in passive anaphylaxis.** E. FRIEDBERGER AND V. SCIMONE. *Z. Immunitat.* **30**, 386-94 (1923); cf. *C. A.* **17**, 2316.—In passive anaphylaxis only that part of the precipitation which ppts. loosely and deviates complement, that is, the isogenetic precipitin, prepares the animal. The heterogenetic precipitin, which is scarcely concerned with complement deviation, plays no role in sensitizing for passive anaphylaxis. These facts are an argument for the essential significance of complement in anaphylaxis. E. R. L.

**Glucolysis in diabetic and non-diabetic blood.** W. DENIS AND UPTON GILES. *J. Biol. Chem.* **56**, 739-44 (1923).—"Glucolysis in normal blood is much more active than in the blood of persons suffering from fairly severe diabetes. In the blood of 2 persons dying from diabetic coma practically no glucolysis took place even after standing for 24 hrs. These findings are explained on the assumption that in normal subjects the 'blood sugar' consists of  $\gamma$ -glucose which is readily attacked by the glycolytic enzyme, while in persons suffering from severe diabetes probably only a small portion of the reducing bodies consist of  $\gamma$ -glucose, the main portion being  $\alpha$ d form which the glycolytic enzyme is powerless to attack. The amt. of glucolysis obtained bears no relation to the concn. of the blood sugar, a point suggesting the fact that in diabetes the qual. compn. of the blood sugar may be entirely independent of its quant. relations." A. P. LOTHROP.

**The differential diagnosis between benign and malignant glucosuria by means of intravenous injections of small quantities of grape-sugar.** STEFAN JØRGENSEN AND TAGR PLUM. *Acta Med. Scand.* **58**, 161-200 (1923); cf. *C. A.* **16**, 3365. Blood sugar curves after intravenous administration of glucose seem to be much more characteristic than the curves obtained by peroral loading-tests. After intravenous injection of 20 g. glucose the highest content of blood sugar is found immediately at the termination of the injection. In normal subjects the blood sugar falls very rapidly, the normal level is reestablished in less than 90 min., and a distinct hypoglycemia appears as an after-effect. The area of the time curve is less than 60 cm.<sup>2</sup>. In diabetics also the blood sugar following an intravenous injection of 20 g. glucose falls very rapidly in the beginning, but later the curve becomes broader, uneven, and serrated. The area of diabetes curves is over 60 cm.<sup>2</sup> and none of the diabetics restores the blood sugar to fasting value in less than 2 hrs. In patients with glucosuria of benign origin the blood-sugar curves were normal. Expts. with the intravenous injection of glucose into children are opposed to the idea that the carbohydrate tolerance is proportional to the body weight. On the contrary, the tolerance for carbohydrate per kg. is more nearly inversely proportional to the body wt., i. e., it seems to decrease with age. Glucosuria following the intravenous injection of 20 g. glucose is insignificant even in diabetics, the excretion of the sugar by the kidneys being of little consequence in the blood-sugar regulation. The latter is supposed to take place in 2 phases, especially well marked in diabetes curves: (1) the regulation of the blood sugar is due to its distribution between the blood and the body fluids; (2) following this, other processes (transformation into glycogen, combustion, etc.) become active. It is the last portion of the blood-sugar curve corresponding to the 2nd phase that is characteristic in diabetics. S. MORGENTHAU.

**The sensitization of salts through globulins as affecting the precipitation of gold solutions.** G. H. FISCHER AND A. FODOR. *Kolloid Z.* **32**, 279-84 (1923).—"To explain the mechanism of the colloidal gold reaction on cerebro-spinal fluids expts. were performed to answer the questions (1) what effect has the H-ion concn. on colloidal Au pptn. by globulin solns. contg. either large or small amts. of salt; (2) are the globulin particles pptd. along with the colloidal Au, or is the elec. charge of the globulins destroyed by the salt present? Globulin pptd. from blood serum and carefully dialyzed with increasing alkali additions for one series and of NaCl additions for a 2nd series and gold solns. pptd. according to the method of Castoro were employed. The pptg. action depends on the dehydration of the globulins and, therefore, on the magnitude of the salt addition. Five cc. globulin with 5 cc. Au soln. after 24 hrs. were filtered and electrolyzed and the N was detd. in the negative and positive chambers by the Kjeldahl method. Nearly equal N detns. indicate either no union between Au and globulin, or a displacement of the globulin by the salt. Dehydrated globulin pptd. with CO<sub>2</sub> impedes the Au reaction. A. MUTSCHLER.

**Calcium content of the blood in premature-birth rachitis with special consideration of craniotabes.** TOIVO TYRNI. *Ann. acad. sci. Fennicae* 16A, No. 4, 65 pp. (1920).—In the healthy newborn during the first days of life the Ca content of the blood is greater by about 1.8 mg. per 100 cc. of serum than the Ca content of older infants or adults. By the middle of the first month the Ca content of the serum is reduced to the normal child and adult figure, which varies between narrow limits and is usually 17.6 mg. CaO per 100 cc. of serum. In the prematurely born those a few days old have about 19.5 mg. CaO in 100 cc. of serum, this amt. being independent of the body size at birth. After about 15 days the Ca content falls to the normal figure. Soon, however, in the prematurely born the Ca content of the blood begins to rise. Hereby is established an evident connection between the origin of craniotabes and other rachitic symptoms and the rise of the Ca content of the blood. The craniotabes and Ca content both reach their max. (21.75 mg. per 100 cc. of serum) in the course of the third month. During the 4th to 5th month the Ca content of the blood of the prematurely born decreases. At the same time there is also an abatement and disappearance of the craniotabes. In 7 to 8 months the Ca content is about normal. This discovery indicates that the incapacity of the bones to assimilate Ca is the origin of rickets. Apparently the absorption of Ca from the alimentary canal is not reduced.

L. W. RIGGS

**Importance of calcium and of potassium in the pathologic physiology of cancer.** MAURICE WOLF. *Compt. rend.* 176, 1932-4 (1923).—This study, which is mainly histological, leads to the following conclusions: Cancerous tissue presents an exaggerated permeability to Ca and K as compared with normal tissue. That Ca and K play an important role in the pathologic mechanism and evolution of cancer, is perhaps explained by their antagonism to electronic radiation. The capacity for exptl. resorption by cancerous tissue in the mouse is for K 3 times and for Ca 20 times the initial content. These figures have been obtained by chem. analysis of cancerous human tissue. The simultaneous accumulation in variable and independent quantities of K and Ca controls the vital rhythm or proliferatory activity of the cancerous tissue. Ca appears to be capable of acting efficiently only in its ionic form. It is suggested that the physical radiation treatment of cancer be combined with the physicochem. treatment by ionic Ca.

L. W. RIGGS

**Antienzymes.** E. ABDERHALDEN AND R. WERTHEIMER. *Fermentforschung* 6, 286-301 (1922).—Various enzyme preps. (polypeptide-splitting enzyme of the pancreas and yeast, liver diastase, pancreatic lipase and yeast saccharase) were administered intravenously to rabbits and the serums were subsequently tested for the presence of antienzymes. All results were negative. When invertin solns. were placed in tested membranes the enzyme was found not to dialyze.

R. L. STEHLE

**Mechanism of the so-called Abderhalden reaction. X. Influence of toluene, chloroform and phenol on the physicochemical properties of blood plasma and serum.** E. ABDERHALDEN. *Fermentforschung* 6, 340-4 (1922); cf. *C. A.* 17, 778.—The compds. in question alter plasma and serum slightly. In carrying out the Abderhalden reaction the amt. of PhMe should not exceed 0.5 cc. and should be const. in quantity in comparative tests.

R. L. STEHLE

## H—PHARMACOLOGY

ALFRED N. RICHARDS

**Oxalic acid poisoning.** S. A. BROWN AND A. O. GETTLER. *Proc. Soc. Exptl. Biol. Med.* 19, 204-8 (1922).—A man aged 44 had taken 4 to 4.9 g. oxalic acid mixed with  $MgSO_4$ . Chem. examn. of the blood showed a marked increase of the excretory products, reaching the max. in 10 days and returning to normal in 28 days. Recovery was good excepting for the damage done to the gastric mucosa.

C. V. BAILEY

**Further observations on anaphylactoid phenomena from different agents, including histamine.** P. J. HANZLIK AND H. T. KARSNER. *Proc. Soc. Exptl. Biol. Med.* 19, 302-3 (1922).—Of the 25 different agents injected intravenously into guinea pigs, the following caused anaphylactoid symptoms: colloidal As, kaolin, blood charcoal, colloidal Fe, 10% NaCl (?), tragacanth, toxified agar, lung ext., glacial AcOH,  $CuSO_4$ , Na oxalate, Na citrate, tannin, tartar emetic, and histamine (0.00011 mg. per g. of animal). All, excepting the chloride and citrate produced pulmonary thrombosis. Histamine caused agglutination of human, avian, guinea pig, dog, and cat red blood cells *in vitro*. The following caused no anaphylaxis: caramel (50 percent), cane sugar, casein, Ca lactate, lutein ext., horse serum, and colloidal Au (sensitive). Hypertonic solns. of cane sugar and of NaCl did not prevent nor cure anaphylaxis. Intraperitoneally, the various substances produced no results, excepting  $CuSO_4$ , which caused anaphylactoid symptoms and death in 40 min.

C. V. B.

**Urinary excretion of salicyl after the administration of salicylate and salicyl esters.** P. J. HANZLIK, F. DE EDS AND E. PRESKO. *Proc. Soc. Exptl. Biol. Med.* **19**, 303-4 (1922).—Doses of 0.05-1 g. of Me salicylate, acetylsalicylic acid, and salicylsalicylic acid (diploal) were given to human subjects and their excretion was compared with that of Na salicylate. The mean total excretion of Na salicylate was 80% and the time 48 hrs.; that of salicyl following the administration of the esters was 60% in 48 hrs. Me salicylate required 55 hrs. and the urine contained unchanged esters. C. V. B.

**The effect of administration of arsphenamine in combination with various colloid substances on its toxicity.** J. OLIVER AND S. S. YAMADA. *Proc. Soc. Exptl. Biol. Med.* **19**, 304-5 (1922); cf. *C. A.* **16**, 1922.—The addn. of 3% gelatin to intravenous injections of arsphenamine prevented the immediate or "physical" ill effects and greatly lessened the delayed or "chemical" toxic effects on the liver and kidneys. C. V. B.

**Detoxication in the organism of the fowl.** C. P. SHILKWIN AND J. H. CROWDER. *Proc. Soc. Exptl. Biol. Med.* **19**, 318-20 (1922).—Phenylacetic acid when fed to chickens is excreted combined with ornithine as phenylacetylornithine. Benzaldehyde (3 g.) was fed to a hen and 0.5 g. of ornithine acid was isolated from the excreta (2 mols. of benzoic acid combined with 1 mol. of ornithine). *p*-Hydroxybenzaldehyde (3.6 g.) was fed to a hen and 1.5 g. of *p*-hydroxybenzoic acid was recovered from the excreta. Phenylpropionic acid was excreted as benzoylornithine and free benzoic acid. Cinnamic acid underwent reduction to phenylpropionic acid and then oxidation to benzoic acid; 0.5 g. benzoylornithine was recovered from the excreta after the administration of 3 g. of cinnamic acid. Nitrobenzene is extremely toxic; 0.5 g. was fed to a hen which died 13 hrs. later; qual. tests were obtained for *p*-aminophenol in the excreta, an oxidation and reduction having taken place. *m*-Aminobenzoic acid, when fed to fowls, seems to undergo acetylation, resulting in the formation of *m*-acetylaminobenzoic acid. C. V. B.

**The effect of sodium benzoate and sodium hippurate, and other drugs on the glomerular circulation in the frog.** R. N. BIETER AND A. D. HIRSCHFELDER. *Proc. Soc. Exptl. Biol. Med.* **19**, 352-3 (1922).—Richard's method of direct observation was used. Na benzoate (0.008 to 0.020 cc. of a 1% soln. per g. frog) caused an increase in the no. of functioning glomeruli, the no. of active loops in each, and the velocity of flow in each capillary. Na hippurate had the opposite effect. Nitroglycerin, theobromine, and Na indigosulfonate increased the glomerular circulation; the last stained the capsule blue, showing its excretion by the glomeruli as well as by the tubules. II. **The effect of phenolsulfonephthalein on the glomerular circulation in the frog.** A. D. HIRSCHFELDER AND R. N. BIETER. *Ibid.* 415-6. The drug was excreted through the glomeruli and tubules. The fluid in the capsule was pink, that in the tubule a deep red, indicating degrees of alkalinity. The tissues surrounding the renal capsules are in some animals stained a diffuse red and in some a light yellow, indicating at times a greater or less alkalinity than  $pH$  7.2. C. V. B.

**Study of adrenaline glucosuria; action of repeated subcutaneous injections of adrenaline on the rabbit.** M. GARNIER AND E. SCHULMAN. *J. physiol. et path. gén.* **21**, 92-103 (1923).—Repeated small doses of adrenaline are usually well withstood, and tolerance to much larger doses (8 to 10 mg.) can gradually be attained by slowly increasing the dose. Such tolerance persists for 2 or 3 months. Animals behave differently to repeated dosage. In some, glucosuria diminishes and disappears, though hyperglucemia persists. In others, hyperglucemia and glucosuria become marked, and then either death ensues or there is a slow return to normal. The hyperglucemia is not proportional to the dose. With normal rabbits initial doses of 8 to 10 mg., though fatal in some hrs., give no greater hyperglucemia than does 1 mg. The increased glucosuria with increasing dosage decreases for every additional mg. A. T. CAMERON.

**The effect of lead on the animal organism with regard to change in the blood.** HEINRICH HÜTTMANN. *Deut. Tierarztl. Wochschr.* **30**, 313-4; *Chem. Zentr.* **1922**, III, 568.—Feeding of Pb to hens in doses of 130 and 100 g. in 13 and 19 days, resp., and 24-8 g. of Pb to ducks in 6 days caused death. PbO fed to hens in doses of 9-30 g. in 3-18 days, resp., and 10-15 g. to ducks in 5 days, and 60 g. in 3 days to a calf also caused death. Ninety g. of impure PbS fed to a hen in 9 days and 120-150 g. fed to ducks in 8-10 days caused no evidence of sickness. A calf died after 5 days' feeding with 150 g. PbS. Polychromasia and basophilic granulation appeared in the blood of hens and ducks, but not in the blood of calves. C. C. DAVIS.

**The behavior of the kidneys in illuminating-gas poisoning.** J. KENNEDY. *Deut. Z. ges. gerichtl. Med.* **1**, 423-39; *Chem. Zentr.* **1922**, III, 794.—The acute CO poisoning of human beings either from toxic injury or from disturbances of nutrition from O deficiency causes an irritation or injury of the glomerulus and the epithelia of the kidneys

as a deep swelling. Deep-seated injury to the extent of disintegration, fatty degeneration or necrosis was observed in no case.

C. C. DAVIS

**The alleged dechlorinating action of calcium chloride.** VITTORIO SUSANNA. *Rif. med.* 38, 146-7; *Chem. Zentr.* 1922, III, 737.—The internal or subcutaneous administration of  $\text{CaCl}_2$  to healthy rabbits seldom causes increased diuresis but usually a considerable temporary increase in the elimination of urea. Increased elimination of Cl depends upon the  $\text{CaCl}_2$  administered.

C. C. DAVIS

**The problem of the antagonism of salts.** L. M. UTIN. *Nachr. Phys. Chem. Lomonossow-Ges. Moskau* 2, No. 2, 1-36(1921); *Chem. Zentr.* 1922, III, 887.—Exptl. evidence is given that the phenomena of *antagonism between uni- and bivalent metals* is analogous to the expts. of Loeb on yeasts. The elimination of the poisonous effect in NaCl soln., produced by a definite Mg salt concn., varies with the NaCl concn. With small amts. of Mg salt, concd. NaCl is more active in depriving the soln. of poisonous effects than dil. NaCl. With increase in the Mg concn. the converse is true. The curves of the protecting Mg concns. are very similar to the corresponding adsorption curves. The adsorption formula of Freundlich can be satisfactorily applied to the antagonism phenomena and support is lent to the theory of Nathanson-Ostwald-Deinöschek. The poison-eliminating action of  $\text{MgCl}_2$  in NaCl solns. is greater than that of  $\text{MgSO}_4$ . The action of large amts. of non-dissociated  $\text{MgSO}_4$  mols. agrees with the theory of Schilow that non-dissociated mols., but not free ions, are essential to the adsorption of electrolytes.

C. C. DAVIS

**Hippuric acid.** G. R. LOVE. *J. Am. Inst. Homeopathy* 16, 120-3(1923).—Hippuric acid in large doses (0.1 to 0.3 g. per kg. of body wt.) stimulates respiration by virtue of its glycine segment, for glycine, in equimol. dosage, exerts the same action. Hippuric acid exerts no sp. pharmacological action upon either the cardiovascular or the smooth-muscle mechanisms. Hippuric acid prepd. from urine may possess a sympathomimetic action by contamination by a pressor substance. These conclusions are based on intravenous administration of Na hippurate to dogs.

J. S. H.

**Pathology and pharmacology of Apis mellifica.** A. G. NAST AND L. J. BOYD. *J. Am. Inst. Homeopathy* 16, 123-34(1923).—A comprehensive review of the compn. and pharmacology of the poison of the honey bee.

JOSEPH S. HERBURN

**Post mortem findings in two cases of hydrocyanic acid gas poisoning.** G. R. S. THOMAS. *Lancet* 1923, I, 1210-1.—The odor of HCN could not be noted on the surface of the body or in the urine. The odor was noticeable in all the serous cavities and strong in the lateral ventricles. Facial lividity, cyanosis of the nails and a marked pink color of the intestines and stomach and aorta, with a green coloration of the liver and of the brain, were among the other pathological findings.

E. R. LONG

**The influence of acids on the contraction of the stomach.** S. KIKKAWA. *J. Kyoto Med. Soc.* 20, No. 1(1923); *Japan Med. World* 3, 139.—HCl,  $\text{H}_2\text{C}_2\text{O}_4$ , and camphoric acids stimulate, while all the other acids tested by K. inhibit the contraction of the stomach. The min. concn. for contraction of the pyloric end of the stomach was 0.001 N HCl, the max. 0.0025. With 0.0033 N acid the contractions were more ample but less frequent. In the fundus the min. concn. for contraction was much higher.

M. E. MAVER

**The influence of acids on the contraction of the intestines.** S. KIKKAWA. *J. Tokyo Med. Soc.* 20, No. 1(1923); *Japan Med. World* 3, 139.—All the acids tried had more or less inhibitory action on the small intestines, but on the large intestines HCl had little inhibitory action, while lactic acid, dil., stimulated the contraction remarkably.

M. E. MAVER

**The organization of chemico-therapeutic research.** ERNEST FOURNEAU. *Chimie et industrie* 9, 1221-8(1923); cf. C. A. 16, 4278.—A discussion of how best to organize it in France.

A. PAPINEAU-COUTURE

**Alcoholism and the behavior of white rats. II. The maze-behavior of treated rats and their offspring.** E. C. MACDOWELL. *J. Exptl. Zool.* 37, 417-56(1923).—"Alcohol in ancestors may modify the behavior of untreated descendants." Cf. C. A. 15, 2507.

C. H. R.

**Studies in protoplasmic poisoning. I. Phenols.** L. F. SHACKELL. *J. Gen. Physiol.* 5, 783-805(1923).—Expts. on *Limnoria lignorum*, a species of *Artemia* and *Cypris* indicate that when equil. in the distribution of phenol between  $\text{H}_2\text{O}$  and the animal is reached, poisoning proceeds with const. velocity. Two criteria of toxicity were used: The time required for initial recovery after a given time in the soln; and the % which died after stated periods in the soln. The value of the velocity const. of poisoning is independent of the criterion adopted provided the criterion measures the intensity of the effect of the poison and not merely the rate of absorption of the poison.

Recovery from paralysis and death by phenol have the same velocity const. Recovery is probably due to a reversal of the mechanism which underlies poisoning. The velocity of poisoning is nearly proportional to the square of the concn. A mass law interpretation of poisoning by phenols is inadequate. Markedly lipin sol. monohydroxy-phenols (phenol, cresols) cause rapid paralysis with slow recovery; markedly water sol. di- and trihydroxyphenols (pyrocatechol, resorcinol, hydroquinone, pyrogallol) produce paralysis more slowly with rapid recovery. Death of tissue cells is detd. by the aggregation of cell proteins. It is assumed that in unpoisoned protoplasm, a factor in the maintenance of dispersion of tissue proteins is the adsorption of lipins at the protein-water interface. The accumulation of lipin sol. phenols in the lipid layer will facilitate the aggregation of tissue proteins while water-sol. phenols will cause less aggregation because they are much less sol. in the lipid layer. A precise method of obtaining the velocity const. of poisoning is given. CHAS. H. RICHARDSON

### I—ZOOLOGY

R. A. GORTNER

The crystalline style as a possible factor in the anaerobic respiration of certain marine molluscs. C. BERKELEY. *J. Exptl. Zool.* **37**, 477-SS(1923). The crystalline style is associated with anaerobic respiration. It possesses oxidizing properties. C. H. R.

The relation between the electrical conductivity of the external medium and the rate of cell division in sea urchin eggs. R. S. LILLIE AND W. CATTELL. *J. Gen. Physiol.* **5**, 807-14(1923).—No relation exists between the rate of cleavage of *Arbacia* eggs and the elec. cond. of the medium except possibly at dilns. of 20-5 vol. % of sea water. In this range, the cleavage rate decreases with a decrease of elec. cond., but the relation is not linear. CHARLES H. RICHARDSON

### 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Notes for food chemists. Rapid estimation of fat in cocoa by optical refraction. PAUL HASSE AND ELISABETH BAKE. *Chem.-Ztg.* **47**, 557-8(1923). Either 2.5 or 5 g. of cocoa powder, according to its fat content, is weighed into a separatory flask, 10 cc. of a mixt. of equal vols. of  $\text{Et}_2\text{O}$  and  $\text{EtAcO}$  is added and the mixt. shaken 1 min., then is allowed to stand until the ether layer is clear or nearly so. The refractometer is brought to a temp. of 15-20° by means of water, when 0.3 to 0.5 cc. of the clear fat soln. is placed in the instrument and a reading taken. The difference between the reading of the fat soln. and that of the ether mixt. is taken as the reading of the fat. A table is used which gives the percentage of fat for every 0.1 in refractometer readings, from 8.0 to 17.9. This table is constructed for 5 g. of cocoa and 10 cc. (8.13 g.) of ether mixt. For any other wts. ( $K$ ) of cocoa and ( $A$ ) of ether mixt., the percentages given in the table are multiplied by the factor  $5A/8.13K$ , or  $0.615A/K$ . Rapid recognition of salicylic acid in wine, fruit juices, etc. *Ibid.* 561-2.—Five cc. of wine or fruit juice is shaken gently with 6 cc. of  $\text{CHCl}_3$  for 0.5 min., the  $\text{CHCl}_3$  layer is allowed to sep. and is then filtered through absorbent paper into a test tube. This clear filtrate is shaken strongly with 1 cc. of  $\text{H}_2\text{O}$  and again filtered through the same filter into a third small tube. To the latter is added 0.5 cc. of dil.  $\text{FeCl}_3$  (1 drop of 10% soln. to 20 cc. of  $\text{H}_2\text{O}$ ); the mixt. is well shaken and allowed to sep. in layers. If the original substance contained 1 mg. of salicylic acid in 100 cc. the top layer will be colored a strong violet-blue. Woy's sugar estimation in chocolate. *Ibid.* 562-3.—Five g. of chocolate is weighed into a 50-cc. volumetric flask, is moistened with denatured alc., then strongly shaken with sufficient warm water to dissolve the sugar. The soln. is cooled to room temp. and 2 cc. of  $\text{Pb}(\text{AcO})_2$  and water to the mark are added. The rotatory power of the clear soln. is then observed in a 200-mm. tube and the sugar estd. by comparison of the readings with values given in a table. L. W. RIGGS

Detection of  $\beta$ -naphthol in soy sauce. C. NAKAI. *J. Pharm. Soc. Japan* No. 491, 17-26(1923).—Distil 100 cc. of soy sauce over a heated sand bath or asbestos in 5 fractions (7 cc. each), and use fractions 3 and 4 for the test.  $\beta$ -Naphthol can also be extd. with 2 vols. of petroleum ether— $\text{Et}_2\text{O}$  (1:1) by shaking for 30 mins. (without petroleum too much pigment goes into the ext.). To this unknown, in a test tube add a little molybdic acid (5 g. of the acid is dissolved in 100 cc.  $\text{H}_2\text{SO}_4$  by heating and cooled to 50°), so that the 2 liquids will not mix. The formation of a purplish red ring at the junct.



tion indicates the presence of  $\beta$ -naphthol. No other preservative likely to be used in soy gives a similar color. It is sensitive to a concn. of  $\beta$ -naphthol as small as 1 in 300,000.

S. T.

**The determination of vanillin in substitute foods.** F. U. *Deut. Parfumerieztg.* **8**, 98-100; *Chem. Zentr.* **1922**, IV, 447.—A survey of various methods leads U. to recommend a substitution of the too volatile EtOH in the refractometric method of Hasse (cf. *C. A.* **16**, 1818) by  $\text{Me}_2\text{CO}$ . 0.1-1% vanillin in  $\text{Me}_2\text{CO}$  causes an increase in refraction at 17.5° of 0.64-6.4 scale units. Mixts. of vanillin with milk sugar give by the use of this process concordant results. Also in the process of Schellbach and Bodinus (*C. A.* **14**, 3484)  $\text{Me}_2\text{CO}$  is of advantage for the extn. of vanillin.

C. C. DAVIS

**Some notes on the determination of protein.** R. B. PORTS. *J. Am. Assoc. Cereal Chem.* **8**, 66-9(1923).—P. gives the results from 21 replies to a questionnaire sent out to 25 chemists. The questionnaire was accompanied by a sample of flour for the detn. of protein according to the method employed by each chemist. The amt. of protein in this sample as reported varied from 10.95% to 10.28%, av. 10.6%. The questions were as follows: (1) What method of nitrogen detn. was used? State the reagents used and the amts. of each. Five variations in methods were reported. The use of Cu tended to give the lowest results. (2) Approx. time of digestion. The time varied from 20 to 90 mins. (3) Approx. time of distn. (4) Capacity and type of flasks used. These varied from long-necked Kjeldahls to globe flasks with short neck also from 800-cc. flasks to 500-cc. flasks. (5) How much correction do you use as detd. on blank? This varied from 0.6 cc. of 0.1 *N* acid to 0. (6) Do you distil your  $\text{NH}_3$  into an excess of acid? This was answered yes, unanimously. (7) What normality of solns. was used? 19 used 0.1 *N* solns. (8) Do you standardize your acid or alkali? 15 standardized the acid, 5 the alkali, and 1 both. Those using an alkali standardization showed a tendency to run lower. (9) State method and reagents used in the standardization. 13 used the  $\text{BaCl}_2$  method, 3 used K-bitartrate in the alkali standardization, 2 used  $\text{Na}_2\text{CO}_3$ , 2 used oxalic acid, and 1 benzoic acid. The chemist using benzoic acid gave the low result of 10.28% protein. (10) Have your burets been standardized with a Bureau of Standards buret? Only 8 had been so standardized.

J. A. KENNEDY

**Of how much value is the protein test?** L. R. OLSON. *J. Am. Assoc. Cereal Chem.* **8**, 91-4(1923).—O. discusses the proteins found in wheat flour and touches on the blending of flours. The protein content is indicative of very little unless accompanied by a statement about the quality of gluten. From the two a good idea of the value of a sample of wheat can be obtained. This is in a greater measure true of the manufd. flour. Bread is the final test of flour.

J. A. KENNEDY

**The physico-chemical properties of strong and weak flours.** IV. **The influence of ash of flours upon the viscosity of flour-in-water suspensions.** R. A. GORTNER AND P. F. SHARP. *J. Phys. Chem.* **27**, 567-76(1923).—The inorg. salts tested depress the viscosity produced by lactic acid in flour-in-water suspensions. The depression is not due to anion or cation nor solely to valence. With suspensions washed free of minerals there is an increase and an equalization of the effect of the monobasic acids. A  $p_H$  value of 3.0 is the optimum for imbibition with acids, while with NaOH and  $\text{Ba}(\text{OH})_2$  the optimum is 11.0. The electrolytes present in the flour have a greater effect in the presence of acids than alkalis. The imbibitional properties of the gluten proteins are best studied in suspensions from which the sol. ash has been removed by leaching.

BURTON G. PHILBRICK

**Texture vs. protein content vs. kernel weight.** W. L. FRANK. *J. Am. Assoc. Cereal Chem.* **8**, 74-82(1923).—Twelve samples of Hard Red Spring Wheat grown in northwestern Ohio in 1918 were used. Each sample was divided into 6 portions. The following detns. were made: number of kernels, wt. per thousand kernels and protein content of each original sample, and of each of the 72 seps. Six degrees and gradations of texture were recognized: dark hard, hard, spotted, mottled, yellow, and starchy. These are described. Numerous tabulated results are given. There is a direct relation between relative texture and protein content. The difference in protein content of dark hard and hard as contrasted with spotted, does not warrant including the latter in the interpretation of dark hard and vitreous, although the spotted group is admittedly superior to other groups more starchy in appearance. The data presented justify the present interpretation of dark hard and vitreous as used in the com. grading of grain. In general, the protein content increases with greater relative degree of hardness, and is less variable in the hard and dark hard groups than in the other groups of less vitreous texture. There is no well defined progressive relation between relative texture and av. wt. per thousand kernels in the samples studied. Low av. kernel wt. is often associated with relatively high protein content. High av. kernel wt. is often associated with

relatively low protein content. When low av. kernel wt. is associated with hard texture, the protein content is relatively high.

**Some observations on the seasonal and sectional changes in Kansas wheat.** R. V. McVAY. *J. Am. Assoc. Cereal Chem.* **8**, 82-6 (1923).—The author gives examples of these changes and offers an explanation for them. He also considers what efforts might be put forth which would help to keep the strength of our wheat crop at a max. and tend to eliminate the yellow berry tendencies.

**Self-rising flour.** L. MOHER. *J. Am. Assoc. Cereal Chem.* **8**, 69-72 (1923).—“Only a little review of the methods of analyses as used in the self rising flour industry.” No bibliography is given.

**Shortening in sweet doughs.** WASHINGTON PLATT. *Baking Tech.* **2**, 216-9 (1923).—The shortening power of fats depends on the percentage of unsatd. glycerides and upon the plasticity of the shortening at the temp. of the mixing. The higher the percentage of unsatd. glycerides, the greater is the shortening power.

**Milk in bread making.** C. B. MORRISON AND G. W. AMIDON. *Baking Tech.* **2**, 210-3 (1923).—Rats fed on bread made with milk as the only liquid constituent thrived better than those fed bread made with milk as only  $\frac{1}{4}$  of the liquid constituent.

**Constitution of milk. The chemical constituents in their relationship to the physico-chemical properties.** C. PORCHER. *Bull. soc. chim. biol.* **5**, 270-96 (1923). A review.

**A study of the “dry period” of the cow.** G. KOESTLER, E. EISER AND W. LEHMANN. *Landw. Jahrb. der Schweiz* **36**, 1047-97 (1922).—This is a study of the milk obtained at the end of lactation and up to the beginning of the colostrum period. Sixteen tables show compn. of milk of several cows during this period.

**Detection of goat milk in cow milk.** A. HEIDUSCHKA AND R. BEYRICH. *Milchzeu. Zentr.* **52**, 37-40, 49-52 (1923).—With the method of Austin (*C. A.* **15**, 3341) carried out as follows 1% of goat milk could be detected. In a specially constructed tube place 20 cc. with 2 cc.  $\text{NH}_4\text{OH}$  (d. 0.91) and heat in a water bath at 50-55° for 1 hr. Shake the tube at intervals during first half hr. Centrifuge 10 min. at 12-1400 r. p. m. Place in the bath for 20 min. and then centrifuge 10 min. The milk must first be skimmed. 1100 samples were tested.

**Studies in sweetened and unsweetened condensed milk.** WM. G. SAVAGE AND R. F. HUNWICKE. Food Investigation Board, London, *Special Report No. 13*, 103 pp. (1923).—**Sweetened condensed milk.**—A chem. and bacterial examn. of canned sweetened condensed milk obtained from the factories and retail dealers in England and in the United States was conducted to det. the causes for spoilage of this product. After a very thorough investigation into the conditions affecting the processing and canning of sweetened condensed milk, it is concluded that the chief sources of spoilage of this product are (a) type of yeast indicated as “A,” which is spherical and produces gas in the canned product; and (b) slow ingress of air into the sealed tins through minute leaks. The chance for contamination of the processed milk at the factory is enhanced by the widespread idea among factory operators that the added cane sugar is sufficient in itself to protect against after-fermentation. This idea was proved to be false in the study. Among the advocated preventions of unsoundness are the following: (1) Sufficient preheating of milk before condensation, (2) cooling of the condensed milk so as to avoid air contamination, (3) special attention to the sanitation of pipe lines each day (live steam or steam under pressure is not sufficient to reduce contamination), (4) immediate canning of the condensed and cooled product, (5) air-tightness of tin containers. **Unsweetened condensed milk (evaporated).**—After a similar thorough examn. of this manufd. product it was found that (a) non-sporing bacilli, especially the more resistant types of micrococci, were concerned with the spoiling of canned evapd. milk, and (b) the admission of air through minute leaks in the tins, makes it possible for dormant forms to multiply and cause decompn. To obviate these conditions in the factories after sanitary methods in the cleaning of the app., and more thorough sterilization of the canned milk are recommended. Since it is very much easier to kill the bacteria in the raw milk than it is in the tins of evapd. product, the preheating of the milk should be most thoroughly accomplished by holding near the boiling point for at least ten min. before evapn. This report is far more extensive and important than this abstract indicates.

**Use of Endo's medium in locating milk contamination.** L. A. BROWN AND EDWIN J. GORT. *Am. Food J.* **18**, 295-6 (1923).—Endo's medium makes possible the detection of *B. coli* in milk, and indication of objectionable contamination. Milk does not nec-

essarily contain *B. coli* and can be produced free from such contamination, which is an index of conditions existing at the dairy or plant producing the product. The test enables Food Officials oftentimes to point out the source of objectionable contamination and is of value in legal proceedings against filthy samples. It is of great value in controlling the efficiency of pasteurization and methods used in the plant. Bacteriol. standards for certified and raw milk are suggested.

H. A. LEPPER

**A new method for the determination of fat in whey-cheese.** YNGVE BUCHHOLZ AND INGOLF SMITH. *Tidsskrift for Kemi og Bergvaesen* 2, 176-80(1922).—Decompose 1 g. of whey-cheese in 15 cc. HCl of sp. gr. 1.124 for about 2 min. Cool and shake with 10 cc. Et<sub>2</sub>O + 40 cc. naphtha, then with 5 cc. + 20 cc., resp., and finally with the same amts. another time, removing the Et<sub>2</sub>O-naphtha layer each time as completely as possible by means of a pipet. Evap. the ext. and dry for 2 hrs. at 95-100°. The naphtha should distil between 30° and 70°. Sometimes the following procedure might be preferred: Weigh 1 g. of the cheese in a Gottlieb tube, add 12 cc. of 20% NH<sub>3</sub> and heat on the steam bath to 75° for 1/2 hr. Cool, add 10 cc. of 96% alc. and heat again for 1/2 hr. to 75°, shaking occasionally during the heating. Cool and shake with a mixt. of equal amts. of EtOH and naphtha, at first with 50 cc., then with 30 cc. and finally with 20 cc. + 5 cc. alc. Evap. and dry as usual. The above mentioned methods gave very accurate results. The common extn. method gave an av. of 1% smaller fat content than the actual value. The exact ratio between Et<sub>2</sub>O and naphtha is very important.

CHR. H. A. SYVERTSEN

**The lime content of milk and its importance in cheese making.** G. KOESTLER. *Schweiz. Milchztg.* 49, Nos. 35, 36, 37, 38, 39, 40, 41, 42(1923).—This is a lecture given to dairy students on the influence of lime content of milk and effect of feed. Tables show compn. of milk and action of rennet and effect of adding Ca salts to milk, on cheese making.

O. L. EVENSON

**The progress of ripening in various kinds of hard cheese.** CHR. BARTHEL AND L. FR. ROSENGREN. *Medd. Centralanstalt. försöksväsendet jordbruks.* No. 219, 16 pp. (1921).—The data presented give little ground for expecting that by present methods of investigation constn. can be established which can be considered as characterizing the stage of ripeness in different kinds of cheese after different periods of time. However, on the whole it may be said that the amt. of water-sol. N in ripe cheese constitutes at least 30% of the total, and a cheese which contains this amt. can be considered ripe. To this there are exceptions. In one variety the water-sol. N was 16.7% and in another over 50% of the total both six months old and ripe.

C. O. SWANSON

**Experiments to produce cheese from sour milk.** E. HAGLUND. *Medd. Centralanstalt. försöksväsendet jordbruks.* No. 223, 17 pp.(1922).—The expts. have shown that sour but not coagulated milk can be used for the manuf. of cheese if the acid is partially neutralized and the milk afterwards pasteurized.

C. O. SWANSON

**The effect on canned foods of industrial waste in the water supply.** E. P. KOHMAN. National Canners' Association, Washington, D. C., *Circ.* No. 4-L, 11 pp.(1923).—Such serious damage has been the lot of some canners during the last season that it has seemed advisable to specify what constitutes a wholesome water supply from their standpoint. These canners had used the same water supply for years, during which time there was no new source of pollution. Moreover, it was the city supply which was passed upon by public health authorities. The foods packed over a period of weeks later proved to be unmerchable. K. briefly discusses the following subjects: (1) Requirements of drinking water. (2) Requirements of canning water. (3) Water contaminated by taste-producing organisms. Their presence disqualifies the water for canning. (4) Water contaminated by industrial waste. The case of a by-products coke plant is cited in detail. Mention is made of several similar cases. (5) Chlorination involved in producing foreign taste. (6) Only certain proportions of phenol and Cl produce taste. Results of numerous expts. on this point are given. (7) Conditions which caused unmerchable products. (8) Necessity for watching water supply. "Water which contains the effluent from a by-products coke plant in any diln. is not a suitable supply for canners. Chlorination of such a water may cause a taste which will make canned food unmerchable. Even though such a water has been used for years with no noticeable effect, it is only a question of time when the right combination of conditions will result in disaster. A chlorinated city water supply is always a source of danger to canners. Chlorine has been found to produce a pronounced taste under conditions other than when the water was polluted by a by-products coke plant. Canners must be constantly on guard lest their water supply contains something which will give them an inferior quality in their product."

J. A. KENNEDY

**The effect of hard water in canning vegetables.** W. D. BIGELOW AND A. E. STE-

VENSON. National Canners' Association, Washington, D. C., *Bull.* No. 20-L, 39 pp. (1923).—*Water*.—Ca and Mg may be removed by appropriate softening methods; the zeolite method is best suited for softening water for canned foods. *Salt*.—A salt should be used which contains less than 0.3% Ca. In order to minimize as much as possible the hardening effect of Ca and Mg, the brine should be made as weak as is possible without material sacrifice of flavor. *Peas*.—The hardness of water used in the preliminary washing of peas for canning, and in rinsing the peas by means of a spray after the blanch, has no appreciable effect on the hardness of the canned product. Blanching peas in a wire basket or perforated pail suspended in a tank of hard water has a pronounced hardening effect on the canned product. In blanching peas in the continuous blancher usually employed by can. canners, the peas first passing through the blancher remove the greater part of the Ca and Mg compds. from the blanch water and thus soften it. These peas are therefore hardened to a greater extent than the peas that are blanched subsequently. When very hard water is employed, and the flow of water through the blancher is considerable, the hardening effect on the peas is proportional in a measure to the flow of water through the blancher. The use of softened water for blanching is advantageous when the hardness of the water supply exceeds 200 p. p. m. The softening of hard water for brining peas is of fundamental value. The hardness of the water and the amt. of Ca in the salt used in brine for canned peas have a pronounced influence on the hardness of the product. The processes now used with peas are necessary for their sterilization. The use of softened water and pure salt in brining peas will therefore not permit the shortening of the processes now employed. *Ripe beans*. The hardening effect of Ca and Mg compds. on dry beans is even greater than on peas. In packing ripe beans, therefore, it may be advantageous to soften water that is only slightly hard. The hardness imparted to ripe beans by the Ca and Mg compds. of hard water or salt may be partly corrected by a long process, but the appearance of a product so treated is sometimes less satisfactory than that of beans treated with soft water and relatively pure salt and given merely the process necessary for sterilization. *String beans*.—Ca and Mg compds. in hard water and salt do not appear to exert a hardening influence on string beans; the softening of water for use with this product does not therefore appear to be of value. *Corn*.—Ca and Mg of hard water and salt do not exert a hardening influence on either cream style or whole grain canned corn. The use of softened water in the brine of cream style canned corn appears to produce a somewhat darker product than the unsoftened water. Its use is therefore disadvantageous. *Beets*.—Ca and Mg in hard water and salt combine with sol. oxalates naturally occurring in beets and sometimes produce a white coating on the surface of the beets. The softening of hard water and the use of relatively pure salt are, therefore, advantageous. Ca and Mg in hard water and salt do not exert a hardening influence on canned beets, at least below a hardness of 350 p. p. m. A study has not been made with water of still greater hardness or with salt contg. a relatively high % of Ca and Mg. J. A. KENNEDY.

**Swells and springers.** W. D. BIGELOW. National Canners' Association, Washington, D. C., *Circ.* No. 6-L, 7 pp. (1923); supercedes *Lab. Bull.* No. 2 (cf. C. A. 8, 3599).—An attempt is made to answer briefly the following questions: (1) What constitutes a "swell" or "springer?" (2) What are the conditions of the product or of the process which might cause the formation of "swells" or "springers?" (3) What food products in this category might be safely and properly used as food? Some of the most important steps of the canning operation are described. A "swell" in canned foods is a can which has undergone decompn. by microorganisms, accompanied by the generation of gas, which first destroys the vacuum and then causes pressure in the can sufficient to bulge the ends. This decompn. is often of putrefactive nature and may be rapid or slow, according to the organisms and temp. Swells are due either to under-sterilization or to leaky cans. A "springer" is a can whose ends are more or less bulged, but in which the pressure is not sufficient to prevent pushing in the ends to their normal position by the fingers. "Springers" are due to the following causes: (1) Pressure from H<sub>2</sub> generated as a result of chemical action of the acid contents on the metal of the container. (2) Imperfect closing of the can. (3) Overfilling of the can. (4) Sealing at too low a temp. (5) Dented cans. Swells should not under any circumstances be used as food. Springers due solely to insufficient exhaust, or to overfilling or improperly sealing the can, are sound and edible in all respects. Their sale on the market in that form should not be permitted. The bulged end is taken by the consumer as a warning sign, indicating decompn. If such are to be sold to consumers they must be so treated as to remove the bulged condition. In the early stages of springers caused by H<sub>2</sub> gas, the contents are in every way suitable for con-

sumption. Springers of this type which have reached an advanced stage may become unsuitable for food because of the metallic taste of the dissolved Fe. Sometimes such cans cannot be distinguished by their outer appearance from a true swell. Springers may be due to the combined action of several of the causes mentioned. J. A. K.

**The fruit-preserve industry in the Piedmont.** C. ZAY. *Stas. sper. agrar. ital.* **55**, 129-35 (1922).—Analyses show the  $H_2O$ , total dry ext., acidity, reducing sugars, sucrose, non-saccharine ext., protein, ash, alkalinity of ash and the  $H_2O$ -insol. matter in preserves, jams and jellies of peaches, currants, plums, grapes, apricots, quinces, cherries and apples. ALBERT R. MERZ

**What constitutes spoiled food?** CHARLES THOM. *Am. Food J.* **18**, 343-5 (1923).—An address discussing spoiled food including principles applicable to food manuf. to produce food which a discriminating consumer knowing its history or handling would not refuse to eat. H. A. LEPPER

**Effect of isolation on *Oidium lactis*.** KATHARINE G. BITTING. *Canning Age* July 1923, 19-20.—*Oidium lactis* is the one of the most prevalent infections of tomato products. Expts. show that it will not only develop in light but also in light under reduced O supply and pressure. It will not develop in a vacuum as formed by pyrogallol and KOH. H. A. LEPPER

**Disinfection in food-products factories.** H. F. ZOELLER. *Am. Food J.* **18**, 247-9 (1923).—The general sanitary conditions of food-products factories are discussed, including the subject of bettering conditions by the elimination of carelessness and by disinfection. Ten chemical disinfectants are discussed and the advantage of NaClO are pointed out. It has no value as a food preservative and should not be used as such. H. A. LEPPER

**The net energy of feed material.** NILS HANSSON. *Kgl. Landbruks-Akad. Handl. Tid.* **62**, 113-36 (1923).—A comprehensive review of the more important investigations on the net energy of different feed materials. C. O. SWANSON

**The removal of alkaloids from lupines.** GERLACH. *Mitt. deut. Landw.-ges.* **38**, 220 (1923).—The process described by Goy (*C. A.* **17**, 2332) for the removal of alkaloids from lupines was recommended by Lohnert over 30 years ago. K. D. JACOB

**Experimental data on the feeding of cattle.** DONATO SCARAMUZZI. *Stas. sper. agrar. ital.* **55**, 109-24 (1922).—Tables are given of mixts. (in pairs) of various fodders, showing the quantities to be mixed for nutritive ratios (digestible albuminoids: digestible fats + carbohydrates) ranging from 1 to 4 to 1 to 12. The quantities of digestible albuminoids, fats and non-nitrogenous exts., the total dry matter and the ratio between the total dry matter and digestible matter are reported for each mixt. The individual fodders are *Trifolium incarnatum* hay, grain straw, bran, oats, carob beans, beans, vetch hay, olive pomace, grape pomace and flax-seed cake. ALBERT R. MERZ

#### Biochemical action of polarized light (BRYANT) 11A.

**Deodorizing cream and butter fat.** E. M. DAVIS. U. S. 1,463,309, July 31. Cream or butter fat is heated with a diluent such as  $H_2O$  or milk to about 77-99° and violently agitated by air passed through the material to remove moisture and effect deodorization.

**Preserving vitamins of cereals.** D. CHIDLOW. U. S. 1,461,703, July 10. The vitamins of the germ or scutellum of wheat are preserved by heating the material to a temp. of about 132° for a sufficient time (usually about 15-20 min. after a preliminary drying at a lower temp.) to render the material immune to destructive action of the air.

**Treating wheat.** C. W. CHITTY and WOODLANDS, LTD. Brit. 191,473, Oct. 12, 1921. Wheat, before milling, is treated with a halogen gas or with a gaseous compd. contg. available halogen, such as  $Cl$ ,  $HCl$ , or phosgene. The wheat is agitated in a drum or worm and 2-4 oz. of commercially pure  $Cl$ , etc., per sack of wheat is introduced. A larger proportion of  $Cl$  may be employed if the treated wheat or flour produced therefrom is to be mixed with untreated material. Cf. 1661, 1901, 8091, 1903, 14,757, 1903, 16,938, 1913 (*C. A.* **9**, 338) and 168,938 (*C. A.* **16**, 448).

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

**Industrial research.** C. E. SKINNER. *Elec. J.* **20**, 241-7, 300-4 (1923).—An address. The examples of "industrial research" commented on at length include in-

sulation, transformer oil, steel for magnetic purposes, iron plating, lightning arrester, electron devices, and the incandescent lamp. C. G. F.

**The future of the chemical industry in Belgium.** G. DALLEMAGNE. *Rev. universelle mines* 17, 253-9 (1923). C. C. DAVIS

**Materials used in industrial arts and their testing.** G. TAUCHMANN. *Provision* 1, 310-3 (1922); *Physik. Ber.* 3, 749 (1922). A. E. STRARN

**Heat economy in the chemical industry.** F. WIRTH. *Die Wärme* 45, 347-8; *Chem. Zentr.* 1922, IV, 660.—The consumption of heat in chem. industries is characterized in general by the maintenance of a definite temp. and amt. of heat, to which end suitable automatic regulation is essential. As a reliable regulator which can be applied to other forms of energy, such as elec., the are regulator in combination with the Ruth heat accumulator is recommended. C. C. DAVIS

**Hints for reducing operating costs by appropriate maintenance of lead-lined vessels.** SALVISBERG. *Chem.-Ztg.* 47, 554 (1923).—The destructive effects of stray currents or of galvanic action can be reduced by proper insulation or by using carefully detd. counter currents of correct amperage and voltage, controlled by suitable instruments. W. C. EBAUGH

**Insoluble soaps of higher fatty acids as electric insulating materials.** TSUNETARO KUIJIRAI, SAKAB UKEI AND BUNZO KITAHARA. *Bull. Inst. Phys. Chem. Res. (Japan)* 2, 302-4 (1923).—Al, Mg, and Ca soaps of satd. and unsatd. fatty acids, such as myristic, palmitic, stearic, oleic, and linoleic acids, etc., were used for the investigation. Metallic soaps of the stearic acid series are superior as heat-proofing insulating materials; especially Ca stearate in olive oil is the best. Metallic soaps of the oleic acid series are superior as soft and water-proofing insulating materials. They are especially suitable for mixing with resins, coal tar, asphalt, petroleum pitch, etc. Formerly only drying oils were used as the insulating materials, but semi-drying or non-drying oils are also utilized for the purpose by changing them into metallic soaps; they are much cheaper. These soaps are used in soln. in volatile org. solvents. K. KASHIMA

**Foam prevention during evaporation. "System Seyffert."** ANON. *Chem. Umschau* 30, 172-3 (1923).—The foaming of liquids during vacuum evapn. is prevented by providing a special tubular heater in addition to the evaporator, the liquid passing rapidly through the heater in the form of bubbles and vapor and thence into the evaporator, where it strikes a baffle-plate which allows the pure vapor to pass on and upward while the liquid portion passes downward and back into the heater. The app. is built for single, double and triple effect each effect possessing its own special heater. P. ESCHER

**Chronic carbon monoxide poisoning.** ANFIN EGBAHL. *J. Am. Med. Assoc.* 81, 282-4 (1923).—Wharen (Univ. N. Dak.) found CO, by the  $I_2O_5$  method, in garages with no motor running during the previous 6 hrs., 0.1 to 0.2%, in a repair shop 0.2-0.3, gas engine lab. 0.2-0.3, boiler room using coal fuel 0.2, forge shop before starting ventilating fans 0.4, after starting fans 0.2, lab. after using 16 bunsen burners for 2 hrs. 0.1. While persons differ in their susceptibility to CO poisoning, 0.05% when breathed for several hrs. will produce symptoms of fatigue and ill-defined indisposition, explained by the lowered amt. of O in the blood. Two tenths % is dangerous. Chronic CO poisoning lowers the resistance to various infections or favors the renewed activity of an old process. CO poisoning is no longer confined to certain industries as the chances of poisoning are universal. L. W. RIGGS

**Health hazard from automobile exhaust gas in city streets, garages and repair shops. The vertical exhaust as a practical measure of amelioration.** YANDELL HENDERSON AND HOWARD W. HAGGARD. *J. Am. Med. Assoc.* 81, 385-91 (1923); cf. *C. A.* 17, 150.—An automobile was supplied with app. to take samples of the air of the streets of crowded areas (N. Y. City and New Haven). These samples, which were taken under different weather conditions and seasons, were carefully analyzed. The CO content in parts per 10,000 ranged from 0.1 to 4.6 with a general av. of about 1.0. The following rules were formulated to define the physiol. effects of CO, the time being expressed in hr. and the CO in parts per 10,000: time X concn. = 3, no perceptible effect; = 6, a perceptible effect; = 9, headache and nausea; = 15, dangerous. To lessen the concn. of CO in the lower layers of the atm. the exhaust pipe should extend to the top of the machine. The feasibility of this suggestion was proved by expts. with automobiles furnished with the vertical exhaust. L. W. RIGGS

**Modern hygiene in the management of chemical industry.** ANON. *Chem.-Ztg.* 47, 549-51 (1923).—An illustrated article on the wash and change rooms, lunch rooms, etc., at the Schaffstaedt works, Giessen. Wood and non-corroding metal replace iron as far as possible. W. C. EBAUGH

**Gravity separation of coal, ores or other materials.** T. M. CHANCE. U. S. 1,462,881, July 24. Composite sepg. mediums for the treatment of coal, ores or similar materials to separate their components are prepd. by mixing substances of different sp. gr. such as magnetic Fe ore sand,  $\text{SiO}_2$  sand and  $\text{H}_2\text{O}$  to obtain a sepg. medium of desired sp. gr. adapted for the particular material to be sepd.

**Drying gases.** E. H. ARNOLD and W. T. WAKEFORD. U. S. 1,463,279, July 31. H and N or other gas to be dried is passed under low pressure into a chamber and through a perforated partition into a second chamber into contact with  $\text{CaO}$  or other drying material while fresh drying material in comminuted form is continuously supplied to the first chamber.

#### 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

**Standard methods of water analysis—interpretation and results.** Am. Ry. Eng. Assoc., *Bull.* 24, 262(1923).—A method is given for a rapid boiler analysis based entirely on volumetric methods with exception of total solids. The A. P. H. A. method is recommended for full and complete examn. R. C. BARDWELL

**Colorimetric determination of nitrates in water.** B. LAMPE. *Wochschr. Brau.* 39, 303-4(1922).—The following simple modification of Grandval and Lajoux's method for estg. nitrates in water is not affected by the presence of nitrite or of org. matter in the small proportions usually found in natural water. An Erlenmeyer flask contg. 30 cc. of the water is weighed and the liquid then boiled with the amt. of Ag sulfate soln. necessary to ppt. the chloride present. After being cooled, the flask and its contents are made up to the original weight and the soln. is thoroughly mixed. The soln. is then filtered through a dry filter paper until clear, 25 cc. of the filtrate is evapd. to dryness in a porcelain dish on a water bath and the residue mixed by means of a flattened glass rod with 15-20 drops of a reagent prepd. by mixing 0.75 g. of pure phenol with 9.25 g. of pure, concd.  $\text{H}_2\text{SO}_4$ . The contents of the dish are transferred to a 200-cc. flask, mixed with 10 cc. of 10%  $\text{NH}_3$  soln., and made up to vol. In presence of nitrate the soln. is colored yellow by the formation of  $\text{NH}_4$  picrate. A solution contg. 3.844 g. of  $\text{KNO}_3$  per l. is prepd., 10 cc. of this is diluted to 200 cc. and 25 cc. of the diluted liquid evapd. to dryness, treated with the phenol- $\text{H}_2\text{SO}_4$  reagent as described above, and made up to 500 cc. after addn. of  $\text{NH}_3$ . For comparing the colorations, use may be made of a series of similar flasks such as are employed for comparing the colors of worts. If a cell 20 mm. thick, contg. a soln. of 25 g. of  $\text{CuSO}_4$  in 100 cc. of water, is used as a screen, the accuracy of the comparison is increased. J. S. C. I.

**The determination of carbon dioxide and oxygen in steam from various softening processes.** SCHIEDT and STOCKMANN. *Arch. Warmewirtschaft* 4, 7-10, 24-6(1923).—Data include analyses of feed-water of and steam from various points, for 4 plants. Typical values for  $\text{CO}_2$  and  $\text{O}_2$ , resp., in g. per ton of steam, are as follows: lime-soda process, 12, 5; the same, with blow-off water returned to feed, 37, 4; permutite softener, followed by degasifying, 62, 1; no softening, 68, 4. Much of the  $\text{CO}_2$  comes from the hydrolysis of  $\text{Na}_2\text{CO}_3$ . In sampling, the condensate must be collected under oil, as it greedily absorbs  $\text{O}_2$  from the air. ERNEST W. THIELE

**Bacteriological study of the water of Lake Mendota.** F. C. WILSON. *Abstracts Bact.* 5, 11-2(1921).—The water is stratified during the summer, and the lower strata show a lack of free  $\text{O}_2$ . During slight thaws of late winter or early spring, org. matter is carried under the ice. The bacterial count per cc. ranges from approx. 100 in winter to 3550 in early summer. The type of bacterial flora varies with the season of the year. JOSEPH S. HEPBURN

**New features incorporated in water-softening plants.** C. R. KNOWLES. *Railway Eng. and Maintenance* 19, 273(1923).—A new type of conical-bottom steel tank for water-softening plants is featured with full description of operation and results. The chief advantage of such tanks is claimed to be the method for sludge removal. R. C. BARDWELL

**Public water supplies in Pennsylvania.** ANON. *Eng. News-Record* 90, 1002 (1923).—Of the 650 public waterworks in Pennsylvania 410 had either filtration or chlorinating app. in 1922. Only 7% of the urban population is supplied with untreated water, 70% with filtered and 23% chlorinated only. FRANK BACHMANN

**How the Illinois Central handles its water service.** D. A. STEEL. *Railway Eng. and Maintenance* 19, 182(1923).—Description of water service is given including maps, illustrations and charts showing results of typical installations. The saving from water

reatment exceeds \$220,000, per yr. from the removal of 2,425,900 lbs. scale from over one billion gals. water.

**The removal of phenols from the waste waters of mining.** R. C. BARDWELL, W. GLAUD AND R. SCHONFELDER. *Ber. ges. Kohlenforsch.* 1, 161-8; *Chem. Zentr.* 1922, IV, 697.—It is recommended that waste waters of mines be extd. with solvent naphtha. Expts. were carried out in the lab. with tap H<sub>2</sub>O contg. 1% of PhOH. Further expts. are necessary to insure satisfactory results on a large scale. The extn. app. used is described and illustrated.

**Phenol contamination of public water supplies.** ASON. *Eng. News-Record* 90, 128 (1923). Contamination of water supplies by phenols from by-product coke ovens, gas and tar products works is increasing. Chlorination of waters contg. phenols gives offensive tastes and in one case in Ohio chlorination was abandoned because of taste with loss of protection to health. Two preventive methods have been considered: the elimination of the wastes from public water supplies, and attempts to remove the phenols from these wastes. The latter has been successful at some plants by using the coke quenching pits. Objections to this method are odors around the coke plant and the discoloration of the coke. Legal action is doubtful as regards results until damage to health is proved.

**Los Angeles sewage disposal plans assuming final form.** W. T. KNOWLTON. *Eng. News-Record* 90, 1000-1 (1923).—Trunk sewers and ocean outfall are under construction. The sewage before discharge into the ocean will pass through drum screens and the screenings will be removed by elevators to beds where they will be covered.

**Abatement of industrial stenches by means of activated carbon.** A. B. RAY AND F. K. CHARNY. *Chem. Met. Eng.* 28, 1114-6 (1923).—Gases from closed kettles in a rendering works were forced through a water spray chamber and the condensed water run into the sewer. The cooled gases and fumes with or without drying were then passed up through a tower contg. granular activated C, and out into the atm. The C used was a highly activated coconut charcoal, 8-14 mesh. This has a high absorptive power, selecting org. and odoriferous substances in preference to water vapor. It is mechanically strong and so resists crushing and abrading and being relatively dense a min. vol. has a max. absorptive efficiency. The C is revived by heating, preferably by passing steam through it at 15 to 25 lbs. pressure, the condensate from this operation being run into a sewer and the uncondensed steam and fixed gases conveyed into a furnace and burned as fuel. The app. is simple to construct, economical to operate and efficient in action.

**Separation of bacteria by filtration with Zsigmondy-Bachmann membrane filters.** MEYERINGH 11C. The effect on canned goods of industrial waste in the water supply [KOHMAN] 12.

**Purifying water.** H. J. MACRATH. *Brit.* 191,504, Dec. 22, 1921. Portable app. for treating H<sub>2</sub>O with zeolites or other reagent and for which no permanent connections are necessary comprises a container for the reagent having a flexible inlet or outlet pipe by means of which the H<sub>2</sub>O can be passed siphonically through the container, the siphon action being started by pushing a closely fitting plug or stopper into the container.

**Removing air and other gases from water.** R. N. EINHART. U. S. 1,463,158, July 31. A portion of H<sub>2</sub>O or other liquid from which gases are to be removed is evapd., vapors and gases evolved are exhausted through a condenser and the exhaustor is operated so as to maintain the rate of evapn. substantially const. *Cl. C. A.* 16, 980.

**Preventing incrustation in boilers.** G. A. HENRIQUES. *Brit.* 191,449, Oct. 10, 1921. A boiler compd. comprises a soln. of Na carbonate and citric acid, with or without the addn. of tannin. Preferable proportions are 2 lbs. of soda, 5 oz. of citric acid and 1 oz. of tannin.

**Boiler-scale remover.** C. H. HOPPE. U. S. 1,462,550, July 24. A mixt. for preventing excessive scale in boilers is formed of horn 15 lbs., Na<sub>2</sub>CO<sub>3</sub> 1 lb., Ca phosphate 3 oz. and coal tar 1 gal.

**Apparatus for incinerating garbage and sewage.** J. C. CURRY. U. S. 1,463,761, July 31.



## 15 - SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Soil acidity as measured by sugar inversion, the Truog test and the hydrogen-ion concentration and its relation to the hydrolysis of ethyl acetate. F. W. PARKER AND O. C. BRYAN. *Soil Science* 15, 99-107(1923).—A fair correlation was found between the acidity of 42 soils estd. with the H electrode, the Truog test and the inversion of sugar. Acid silicates in the solid form caused the greater part of the inversion of sugar in acid soils. The presence of acid silicates did not, however, catalyze the hydrolysis of ethyl acetate in soil suspensions. R. BRADFIELD

A method for the determination of "active" aluminium in acid soils. PAUL S. BURGESS. *Soil Science* 15, 131-6(1923).—A 100-g. sample of the air-dry soil is shaken for 1 hr. with 500 cc. of 0.5 N acetic acid. The suspension is allowed to settle overnight and the supernatant liquid filtered through a Pasteur-Chamberlain filter. The  $\text{SiO}_2$  is dehydrated and removed in the usual manner and the sol.  $\text{Al}_2\text{O}_3$  detd. by a modification of the Carnot Al phosphate method. Fair correlations were obtained between "active aluminium" detd. in this way and the growth of crops sensitive to sol. Al and also to the "lime requirement" of the soils as detd. by the author's modification of the Jones method. R. BRADFIELD

Aeration of soil as an ecological factor. R. LARS-GUNNER. *Medd. Statens Skogsförsöksanstalt* 19, 125-359(1922); *Bull. Agr. Intelligence* 13, 1435-6.—The results of quant. expts. on aeration and the relation between O and  $\text{CO}_2$  in soils, as well as the factors influencing them and their relation to plant growth, are presented and discussed in detail from a physical viewpoint. P. R. DAWSON

Studies on the toxic properties of soils. A. W. BLAIR AND A. L. PRINCE. *Soil Science* 15, 109-29(1923).—Soils which had become toxic by applications of  $(\text{NH}_4)_2\text{SO}_4$  for 15 yrs. were leached with  $\text{H}_2\text{O}$  and the leachings analyzed for Fe, Al, Ca and other constituents. The leachings from the half of the plot which had been limed contained only a trace of sol. Al and Fe while the unlimed half contained large quantities of both. More  $\text{H}_2\text{O}$ -sol. Ca was found in the unlimed plot. Leachings from these plots were also used as culture mediums for growing barley seedlings. The ext. from the limed plot gave normal growth, that from the unlimed half produced stunted plants.  $\text{NaNO}_3$  and small amts. of sol. phosphates did not overcome this toxicity. Larger quantities of phosphates and lime were effective. Boiling the toxic ext. with  $\text{NH}_4\text{OH}$  and filtering out the Al and Fe gave normal growth if a trace of Fe and sol.  $\text{P}_2\text{O}_5$  were added. Barley plants thrived in normal soil exts. with  $p_{\text{H}}$  values as low as that of the toxic ext., which indicates that the toxicity of the soil is due to the sol. Al rather than the  $p_{\text{H}}$  values. R. BRADFIELD

The biological fixation of atmospheric nitrogen. GEORGES TRUFFAUT. *Chimie et industrie* 9, 1094-108(1923).—A discussion of the mechanism of ammonification and of the benefits derived from partial sterilization of the soil by means of disinfectants, especially by means of  $\text{CaS}$  (cf. C. A. 13, 631). A. PAPINEAU-COUTURE

Buffer action of bicarbonates and their importance on forest soils. F. RAMANN. *Z. Forst- u. Jagdwesen* 4(1922).—The presence of bicarbonates in the soil diminishes the decompn. of other bases, chiefly because of the equil. which exists between the ions in soln. and the undissociated mols. As a result of this buffer action the weathering of mineral particles by the "free  $\text{CO}_2$ " is retarded. In the accumulated litter of forest soils considerable quantities of bases are returned to the soil as bicarbonates. The steady increase in bicarbonates in the soil under the forest litter largely prevents the decompn. of the upper soil layers. The action of all weak acids which form strongly ionized salts (e. g., humic acids) is probably similar to the above. J. S. C. I.

The effect of gypsum on Iowa soils. L. W. ERDMAN. *Soil Science* 15, 137-55(1923); cf. C. A. 16, 2948.—The  $\text{H}_2\text{O}$ -sol.  $\text{P}_2\text{O}_5$  and  $\text{K}_2\text{O}$  of some soils was increased by applications of 200 lbs. per acre of  $\text{CaSO}_4$ ; with 2000 lbs.  $\text{CaSO}_4$  per acre all soils gave large increases in sol.  $\text{K}_2\text{O}$ . Ammonification, nitrification and azoification were only slightly affected by gypsum.  $\text{CO}_2$  production was not hastened except in a highly basic soil. In field expts. the yield of clover and small grains was increased in many cases. Alfalfa was distinctly benefited. Analyses of rain and drainage waters show that the amt. of S lost in the drainage is far greater than that gained in the rain water. A permanent soil-fertility system must provide for the maintenance of its S content. R. BRADFIELD

Relations between calcium carbonate, certain fertilizers and the soil solution. F. W. MORSE. *Soil Science* 15, 75-92(1923).—A theoretical discussion of the soly.

product is followed by exptl. data from soils which have received various lime and fertilizer treatments for the last 23 yrs. at the Mass. Agr. Expt. Sta. A fair correlation between theoretical calcs. and exptl. observations was obtained. When solid  $\text{CaCO}_3$  exists in the soil in contact with the soil soln., the concn. of  $\text{CaCO}_3$  in soln. depends upon the partial pressure of the  $\text{CO}_2$  in the soil air and is independent of the amt. of  $\text{CaCO}_3$  in reserve.  $\text{CaSO}_4$ , Ca phosphates and  $(\text{NH}_4)_2\text{SO}_4$  lowered the concn. of  $\text{CaCO}_3$  in the soil soln. and lessened its alk.,  $\text{NaNO}_3$  and KCl increased the concn. of  $\text{CaCO}_3$  and the alk. of the soln. Superphosphates and KCl had little effect on the  $\text{pH}$  value of unlimed plots.  $(\text{NH}_4)_2\text{SO}_4$  lowered it.

R. BRADFIELD

The applications of potassium fertilization. O. ENGLER. *Ernährung d. Pflanze* 18, 65-7; *Chem. Zentr.* 1922, III, 307.—A survey of approved methods of using K fertilizers in general and the choice of individual K salts for various types of soil and plants.

C. C. DAVIS

The effect of various potassium salts in simultaneous fertilization with various nitrogen fertilizers. HJ. VON FEILITZEN AND E. NYSTROM. *Masskulturverningens Svenska Tids.* 1921, 145; *Chem. Zentr.* 1922, III, 307.—The effect of kainite, 37% K salt and KCl in combination with  $\text{NaNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CaCN}_2$  and without addn. of N in swampy soil (which had received no K fertilization for several yrs.) was investigated. The yields of barley, flax and rye grass were not essentially different with the different forms of K fertilizer and their combination with Na-free and Na-contg. N fertilizers.

C. C. DAVIS

Availability of potassium in orthoclase for plant nutrition. D. E. HALEY. *Soil Science* 15, 167-80 (1923).—The availability of the K in orthoclase was studied by measuring its absorption by buckwheat plants grown in sand cultures. 25-, 50- and 75-g. portions of 200-mesh orthoclase were intimately mixed with 2750 g. of quartz sand to which the other necessary nutrients were added in sol. form. 25 g. of orthoclase yielded 282.2 p. m. sol. K in distl.  $\text{H}_2\text{O}$ . The availability of the K was estd. from the dry wts. of the buckwheat plants and from the amts. of K absorbed when orthoclase was the only source of K as compared to the absorption of sol. K. 50-g. portions of orthoclase supplied K at a sufficiently rapid rate to satisfy the requirements for a 7% larger yield of dry matter than was obtained with the complete nutrient soln. The total amt. of K absorbed from orthoclase was in no case as large as with the complete nutrient soln. but it was apparently utilized more economically.  $\text{CaCO}_3$  and especially  $\text{CaSO}_4$  increased the availability of K. The effect of Na salts was only slight. Dextrose and starch reduced both the wt. of dry matter and the amt. of K absorbed.

R. BRADFIELD

Adsorption and replacement of plant food in colloidal oxides of iron and aluminium. D. C. LICHTENWALNER, A. L. FLENNER AND NEIL E. GORDON. *Soil Science* 15, 157-65 (1923).—Cations were adsorbed by both  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  hydrogels in the order  $\text{Ca} > \text{Mg} > \text{K}$ , the anions in the order  $\text{P}_2\text{O}_5 > \text{SO}_4 > \text{NO}_3$ . The adsorption was specific and the amt. of adsorption increased with an increase in the concn. of the salt. The adsorption of the cation depended upon its accompanying anion. The converse was true out to a less degree.  $\text{NO}_3$  and  $\text{SO}_4$  were entirely leached from the gels with distl.  $\text{H}_2\text{O}$ . With  $\text{P}_2\text{O}_5$  only about  $1/4$  could be removed by leaching. Only the  $\text{H}_2\text{O}$  leachable fraction followed the adsorption isotherm. Chemical forces were probably responsible for the retention of the non-leachable fraction. The non-leachable  $\text{P}_2\text{O}_5$  was available to plants.

R. BRADFIELD

The possibility of a partial replacement of phosphoric acid by silicic acid in plants. TH. PFRIFFER. *Mitt. deut. Landw.-ges.* 38, 196-8 (1923).—The theory is advanced that the increase in yields of straw and grain from plants receiving joint applications of silicic acid, particularly in the colloidal form, and  $\text{P}_2\text{O}_5$  is due to the ability of the former partially to replace the latter in inorg. combinations present in the leaves and stalks, just as K may be partially replaced by Na under similar conditions. The  $\text{P}_2\text{O}_5$ , which otherwise would remain in the stalks and leaves as inorg. compds., is utilized in the increased production of grain or seed and is converted into org. forms. Silicic acid is not able to replace  $\text{P}_2\text{O}_5$  in org. combination in grain or seed. Expts. of a no. of investigators are cited in support of this theory.

K. D. JACOB

The applicability of mineral phosphates to direct fertilizing. HERMANN HILBERT. *Chem.-Zig.* 47, 525-7 (1923).—A review.

P. R. DAWSON

Fertilizing value of pyrophosphates and metaphosphates. Y. KIDA. *J. Sci. Agr. Soc. (Japan)* No. 245, 61-114 (1923).—Although com. fertilizer contains hardly any pyro- or metaphosphate, the phosphates prepd. by a fusion method, such as Jähne's process, consist partly or wholly of these forms; furthermore heating of the orthophosphate, often practiced, produces varying amts. of the pyro- and meta-forms. Expts. whereip barley, oats and wheat were grown in pots with  $\text{Na}_2\text{HPO}_4$ ,  $12\text{H}_2\text{O}$ ,  $\text{Na}_2\text{P}_2\text{O}_7$ .

and  $\text{NaPO}_3$  in Knop's culture medium, showed the same nutritive values for  $\text{P}_2\text{O}_5$  and  $\text{PO}_4$  as for  $\text{PO}_4$ . Further expts. with radishes, carrots, rice, buckwheat, oats and barley, in which  $\text{CaHPO}_4$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{Ca}_3\text{P}_2\text{O}_7$ ,  $\text{Ca}(\text{PO}_3)_2$ ,  $\text{Mg}_3\text{P}_2\text{O}_7$ ,  $\text{Mg}(\text{PO}_3)_2$ ,  $\text{Na}_4\text{P}_2\text{O}_7$  and  $\text{NaPO}_3$  were used as sources of P, showed that the fertilizing values of these salts varied as their soly. in  $\text{H}_2\text{O}$ , i. e., in the order  $\text{NaPO}_3$ ,  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{Ca}_3\text{P}_2\text{O}_7$  and  $\text{Ca}(\text{PO}_3)_2$ , the last named being least effective. Furthermore the solubilities of these same salts in  $\text{H}_2\text{O}$  satd. with  $\text{CO}_2$ , 1 and 2% citric acid, and 2%  $\text{HCl}$  were found to vary in the same order, indicating a correlation between the soly. in weak acid soln. and the fertilizing value. The results of expts. with P compds. of Fe and Al are also reported.

S. T.

**Further notes on the growing of wheat in one-salt solution.** W. F. GERICKE. *Soil Science* 15, 69-73(1923).—Wheat seedlings were grown for 4 months in tap water contg. Ca, Mg, Na,  $\text{SO}_4$  and Cl, having an osmotic pressure of 0.1 atm. The water was not renewed but that lost by transpiration was replenished. The plants made good growth for the first 2 months, but there was no top growth during the last 2 months. These starved plants were then transferred to various single-salt solutions having a concn. of 0.01 N. Normal new growth of tillers appeared on the plants placed in  $\text{KNO}_3$  and in the complete nutrient solution. Tillers started on the plants placed in  $\text{Mg}(\text{NO}_3)_2$  but their growth was abnormal. There was no evidence of new shoot growth in any of the solns. that did not contain  $\text{NO}_3$ . New roots started on plants placed in  $\text{KNO}_3$ ,  $\text{CaSO}_4$ ,  $\text{CaHPO}_4$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{MgHPO}_4$  and  $\text{Mg}(\text{NO}_3)_2$ . G. concludes that the fertilizing efficiency of N is not primarily conditioned by the available supply of that element but is affected by the relation of the supply of that element to that of K.

R. BRADFELD

**Charcoal as a source of carbon dioxide in greenhouse culture.** G. HÖSTERMANN AND ALEXANDRA VON RANKE. *Angew. Botanik* 4, 78-80; *Chem. Zentr.* 1922, III, 1105-66.— $\text{CO}_2$  produced by burning charcoal is unsuitable for greenhouse culture, particularly for flowering plants, unless it is completely freed of poisonous impurities.

C. C. DAVIS

**Increased applications of ammonium alum for the blue coloring of hydrangeas.** M. LOEBNER. *Ber. Tätigkeit gartn. Vers.-Anst. Landwirtschaftskammer Bonn* 4-58, 1920-1; *Chem. Zentr.* 1922, III, 306.—The addn. of  $\text{NH}_4$  alum gives a good blue coloration to hydrangeas. It is well to add at the same time mixts. of fertilizer salt. The effect of the alum is still evident the next year.

C. C. DAVIS

**N. P. K. fertilizer. "QUESTOR."** *Gas J.* 163, 368-7(1923).—A criticism of the E. L. Pease process (*C. A.* 17, 2630).

J. L. WILEY

**The effect of leaf-hopper injury on the sugar content of grapes.** D. L. VAN DINE. *J. Econ. Entomol.* 16, 353-7(1923).—Under conditions of high infestation of the vines, the sugar content (Brix reading) of the grape juice furnishes an index of the efficiency of nicotine sprays. Composite samples from Concord grapes showed a difference of 3.78 in favor of the sprayed vines, selected samples a difference of 2.65.

C. H. R.

**Some experiments on poison baits for the European earwig.** B. B. FULTON. *J. Econ. Entomol.* 16, 369-76(1923).— $\text{NaF}$  has an equal or greater toxicity for this insect than  $\text{As}_2\text{O}_3$  and a greater toxicity than  $\text{CaF}_2$  or Na arsenate. Wheat bran sweetened with molasses was attractive; the addn. of amyl acetate did not render it more so. Oat hulls are more attractive than wheat bran. The addn. of glycerol increases the efficiency of the bait.

C. H. R.

**The length of time Aedes calopus (Stegomyia) larvae should be exposed to a film of kerosene.** M. E. CONNOR AND W. M. MONROE. *J. Econ. Entomol.* 16, 380-5(1923).—A 10-min. exposure will kill most of the larvae. Kerosene acts to exclude the O supply and as a toxin; its toxic action is more rapid than its mech. effect.

C. H. R.

**The effect of carbon disulfide on the germination of seeds.** C. J. WILLARD. *J. Econ. Entomol.* 16, 388-92(1923).—Many kinds of seeds were subjected to  $\text{CS}_2$  at 26.7° for various lengths of time. There is a great difference in resistance to  $\text{CS}_2$  injury. Different varieties are very differently affected, perhaps because of the pigment in the seed coat. Large doses applied for long periods are required to produce a marked effect on germination. Injury is not directly proportional to the dose or the time. Aeration of storage bins is unnecessary unless they are air-tight.  $\text{CS}_2$  will not seriously injure most seeds if poured over them during fumigation.

C. H. R.

**Sulfur dust as an insecticide.** A. KELSALL. *Proc. Acadian Entomol. Soc.* 1922, No. 8, 96-101(1923).—Control of apple insects was greatest on trees treated with S-Pb arsenate dust, but there was a considerable though less effective control on trees treated with a mixt. of 90% S and 10% infusorial earth.

C. H. R.

The use of aluminium sulfate in place of copper sulfate in insecticide-fungicide combinations. A. KELSALL. *Proc. Acadian Entomol. Soc.* 1922, No. 8, 8-17(1923).— $Al_2(SO_4)_3$  and lime mixts. have a more feeble fungicidal action and are not quite so effective as repellents for the potato flea beetle as Bordeaux mixt.  $As_2O_3$  can be used with them for biting insects. C. H. R.

Fertilizers. E. L. PEASE. *Brit.* 191,415, July 12, 1921. Peat, coal, shale, and similar carbonaceous materials contg. N are treated with limited amts. of a suitable acid ( $H_2SO_4$  or  $H_3PO_4$ ) and the product is dried to yield a nitrogenous fertilizer. The product may be lixiviated to extract the sol. salts.

Phosphate fertilizers. L. ADELANTADO. *Brit.* 191,129, Oct. 1, 1921. Phosphates are rendered assimilable by treatment with a neutral sulfate in presence of  $H_2O$  and org. matter at temps. of 60-130°. When the phosphate contains alk. materials it is desirable to add a small quantity of  $H_2SO_4$ . The addn. of small quantities of carbonates, if these are not naturally present, is advantageous, since they react with the added acid and so render the mass porous.

## 16 THE FERMENTATION INDUSTRIES

C. N. FREY

Influence of the theories of Pasteur on the fermentation industries. JUAN EF-FRONT. *Chimie et industrie* 9, 1076-93(1923).—A review. A. PAPINEAU-COUTURE

Denaturation problem. HJALMAR JOHANSSON. *Tekn. Tids.* 53, *Kem. Afd.* 29-33(1923).—A technical address on the denaturing of alc. Many substances are mentioned or referred to but dismissed as impractical. HCN and  $CH_3CH=CHCHO$  are commented on in more detail. A. R. ROSE

The determination of volatile acidity of wines using very small samples. PH. MALVEZIN. *Bull. soc. chim.* 33, 849-52(1923); cf. *C. A.* 17, 179.—A method for detg. volatile and total acidity is described. C. N. FREY

The presence of aldehydes in sulfured wines and the aldehydic phase in the alcoholic fermentation of sugar. E. GIACANELLI. *Stat. sper. agrar. ital.* 56, 112-23(1923).—Acetaldehyde is formed as an intermediate product in the fermentation of sugar by yeast. Under ordinary conditions of fermentation it is transformed into alc. The relatively high proportion of aldehydes found in sulfured wines is due to the presence of sulfites and pyrosulfites which combine with the aldehyde to form compds. unaffected by the activity of the yeast. ALBERT R. MERZ

Aldehydes in wines. J. ESTALELLA. *Anales soc. españ. fis. quim.* 21, 33-44 (1923).—Various theories dealing with the formation of aldehydes during the fermentation of wines are discussed. Expts. by E. showed that when a little  $K_2S_2O_8$  is added to the must the amt. of aldehydes formed is greatly increased. L. E. GILSON

Alcoholic fermentation by means of yeast cells under different conditions. VIII. Formation of glycerol when the intermediate aldehyde is adsorbed with animal charcoal. E. ABDERHALDEN. *Fermentforschung* 6, 345-7(1922); cf. *C. A.* 16, 3928.—Previous results were improved by using larger amts. of charcoal. R. L. STEHLER

A study of the separation of the gases formed in the butyl alcohol-acetone fermentation process. E. W. BLAIR, T. S. WHEELER and J. REILLY. *J. Soc. Chem. Ind.* 42, 235-40T(1923).—During BuOH fermentation 100 lbs. maize (65% starch) yields 7 lbs. acetone, 16.3 BuOH, 39  $CO_2$ , 0.9  $CO_2$  (in soln.), 1.1  $H_2$  and 1.2 lbs. fatty acids. The  $CO_2$  formed is equiv. to 350 cu. ft. at 20° and 760 mm. pressure and the  $H_2$  to 200 cu. ft. A study was made of the conditions affecting the soly. of  $CO_2$  and  $H_2$ . The mixt. of gases was passed up 2 towers under 11 atm. pressure, where it met a descending stream of  $H_2O$  cooled to 15°. The entering gas had a compn. of  $H_2$  40%,  $CO_2$  60% and the gas leaving the second tower had a compn. of  $H_2$  95%,  $CO_2$  5%. Upon the assumption that the gas formed passes up a tower, down which  $H_2O$  is flowing, of such size that equil. with the entering gas is obtained by the  $H_2O$  flowing away, and that the 100 cu. ft. of gas used, and the corresponding quantity of  $H_2O$  are taken to be very small compared with the total quantity of gas and  $H_2O$  passing the tower the following equations were developed: Let  $S_1$  = the soly. in cu. ft. at 15° and at the partial pressure of the entering  $H_2$  gas at 15°,  $S_2$  = the soly. in cu. ft. and at the same temp. and pressur. as  $S_1$  of  $CO_2$  at 15° at its partial pressure in the entering gas,  $a$  = quantity of  $H_2O$  in cu. ft. used to treat 100 cu. ft. of entering gas at its own temp. and pressure,  $b$  = % of  $H_2$  in gas entering the tower,  $b_1$  = % of  $H_2$  in gas leaving the tower. Then  $b - S_2a$  is the quantity of  $H_2$

leaving the tower corresponding to 100 cu. ft. of entering gas, and the quantity of  $\text{CO}_2$  is  $100 - b - S_2a$ . Therefore,  $(b - S_2a)/(100 - b - S_2a) = b_1/(100 - b_1)$ , and  $ab_1(S_1 + S_2) = 100aS_1 - 100(b_1 - b) = 0$ . The vol. of the exit gas is  $100 - a(S_1 + S_2)$  cu. ft. From the equations a series of graphs was calcd. giving the quantity of  $\text{H}_2\text{O}$  required at 15° and 11 atm. pressure to wash 100 cu. ft. of gas at 15° and 1 atm. pressure contg. 40%  $\text{H}_2$  and upwards so that the issuing gas may contain any given % of  $\text{H}_2$  up to 100. The amt. of  $\text{H}_2\text{O}$  required to obtain a given % of  $\text{H}_2$  gas leaving the second tower from a given % of  $\text{H}_2$  gas entering it is given in Fig. II. The quantity of  $\text{H}_2\text{O}$  required in the second tower to obtain any final gas with any intermediate gas can be obtained from the equation. Exptl. results indicate that it is impossible to wash in a tower to 100%  $\text{H}_2$ , because of the decrease in partial pressure of  $\text{CO}_2$  as the % present falls. The  $\text{H}_2\text{O}$  flowing away never comes into equil. with the entering gas. 90%  $\text{H}_2$  can be obtained. The quantity of  $\text{H}_2\text{O}$  required in the second tower to produce 90%  $\text{H}_2$  can only be accurately forecast when the entering gas is not above 80%  $\text{H}_2$ . A description of the exptl. plant is given. C. N. FREY

**Accelerating propionic fermentation.** J. M. SHERMAN. U. S. 1,459,959, June 26. The production of propionates and acetates from carbohydrates and salts of organic acids by the use of organisms of the type of *Bacterium acidi propionici* is accelerated by the presence of various organisms which do not themselves produce propionates, e. g., *Lactobacillus casei*, *Proteus vulgaris*, or *Bacterium alcaligenes*.

**Vinegar.** J. D. MONROE. U. S. 1,459,513, June 19. A mixt. of sucrose 50 lbs., "yeast" 1 gal., tartaric or acetic acid 1.25 lbs. is dild. with  $\text{H}_2\text{O}$  and is permitted to ferment for about 36 hrs. and thereafter to "age" for 6 mos. or the "aging period" may be reduced to 10 days by the addition of a portion of finished vinegar. The "yeast" is a prepd. mixt. formed from pure yeast, flour and  $\text{H}_2\text{O}$ .

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

**Contraluesin.** RICHTER. *Arch. Dermat. u. Syphilis* **138**, 243-6; *Chem. Zentr.* **1922**, III, 685.—*Contraluesin* is a colloidal emulsion contg. 0.1 mg. Au amalgam, 0.01 mg. I and 1 mg. As per cc. Its action is explained and favorable clinical results are cited. C. C. DAVIS

**Genesis of hydrocyanic acid in the "pakra" oil used in adulterating mustard oil.** P. NEOGI AND B. B. ADHICARI. *Proc. 7th Indian Sci. Cong.* **1921**, lxxvii.—Mustard oil is largely adulterated with oil extd. from the seeds of *Schleichera trijuga* ("pakra" oil). The injurious effects of such oil are attributed to HCN, which is due to amygdalin accompanied by an enzyme giving the tests of emulsin. The hydrolysis products of the glucoside (PhCHO and glucose) were obtained and both the glucoside and the enzyme isolated. C. C. DAVIS

**The alkaloids of *Lupinus albus*.** J. RANEDO. *Anales soc. españ. fis. quim.* **20**, 527-30(1922).—By the method of S. Davis (*Arch. Pharm.* **235**, 199), a yield of 1.2% crude alkaloid was obtained from white lupine seed. It was slightly levorotatory, but after several recrystns. from petroleum ether it was obtained in optically inactive form, m. 92-5°, b. 360-5° with slight decompn., b<sub>10</sub> 233-4° without decompn. Refluxed with a  $\text{C}_6\text{H}_6$  soln. of MeI it yielded a methiodide, which, recrystd. from EtOH, m. 235°. L. E. GILSON

**Nomenclature in the coming new edition of the Swedish Pharmacopoeia.** HUGO WASTENSON. *Svensk Farm. Tids.* **27**, 193-5(1923).—W. urges the retention of the old nomenclature until an international nomenclature has been created. A. R. ROSE

**Supplement to the French Pharmacopoeia.** P. E. LUNDIN. *Svensk Farm. Tids.* **27**, 206-11(1923).—A critical review of the treatment of 29 medicinal preps. in this supplement. A. R. ROSE

**In what manner can medicinals be best conserved and how may sterile solutions be prepared from them?** HARALD HUSS. *Svensk Farm. Tids.* **27**, 221-5, 238-42(1923).—A lecture. A. R. ROSE

**Studies of the bark of *Myrica cerifera*, Linné.** HEBER W. YOUNGKERN. *J. Am. Pharm. Assoc.* **12**, 484(1923).—Commercial specimens of bayberry bark varied widely in the proportions of root, bark from the rhizomes and aerial stems. Authentic specimens of each kind were studied and their histological characteristics recorded. Tannin is present in all three barks. L. F. WARREN

**Alkaloidal assays of *Delphinium andersonii*, Gray.** M. R. MILLER. *J. Am. Pharm. Assoc.* **12**, 492-3(1923).—Many species of *Delphinium* contain poisonous alkaloids, but no reports were found concerning *D. andersonii*, although the ground parts are known to be toxic to cattle. Leaves and stems were air-dried and  $H_2O$  was detd. Alkaloids were detd. by well known methods and the results calcd. to dry material basis. The values calcd. as delphinine were 1.64, 1.75, 1.76, and 1.90%. L. E. WARREN

The titration of silver ions and chloride ions in the presence of protective colloids (TREADWELL, *et al.*) 7. Ternary system antipyrine-caffeine-water (KREMAN, JANETZKY) 2.

**Synthetic drugs.** ABBOTT LABORATORIES. Brit. 191,122, Sept. 27, 1921.  $\gamma$ -Dialkylaminopropyl esters of benzoic acid or substituted acid are prepd. by condensing the  $\gamma$ -halopropyl ester of benzoic acid, or a substituted benzoic acid, with a dialkylamine in which one of the alkyl groups is greater than ethyl; the products are local anesthetics. The corresponding aminobenzoic esters are made from nitrobenzoic  $\gamma$ -halopropyl esters, the nitro group being reduced, either before or after the condensation with the dialkylamine, electrolytically or with Sn or Fe and HCl.

**Synthetic drugs.** SOC. ANON. POUR L'IND. CHIM. A BALÉ. Brit. 191,233, Nov. 16, 1921. 3,4-Dihydroisoquinoline-3-carboxylic esters are prepd. by hydrogenating  $\alpha$ -acylaminocinnamic esters or their nucleus substitution products in soln. by H in presence of a metallic catalyst and treating the resulting dihydrocinnamic acid derivs. with condensing agents such as  $POCl_3$ ,  $PCl_5$ , or  $P_2O_5$ . The parent  $\alpha$ -acylaminocinnamic esters are produced by heating aromatic aldehydes with acylated glycines,  $AcONa$  and  $Ac_2O$ , and esterifying the resulting lactam. Numerous examples are cited.

**Water-soluble diethylbarbituric acid compounds.** F. QUADE. U. S. 1,461,831, July 17. A soln. of diethylbarbituric acid in  $H_2O$  is digested with freshly pptd.  $MgCO_3$  and the filtered soln. obtained is evapd. to dryness *in vacuo* to obtain a  $H_2O$ -sol. salt adapted for use as a therapeutic agent in mixts. with salts of acetylsalicylic acid.

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

**Researches on the formation of sulfuric acid by the chamber process.** E. BRINER AND M. ROSSIGNOL. *Helvetica Chim. Acta* **6**, 647-55(1923).—With modern app. and gas technic known mixts. of  $SO_2$ ,  $NO_2(N_2O_4)$ ,  $H_2O$ ,  $O_2$  and  $N_2$  were led into a series of glass vessels at a known rate, and the rate of formation of  $H_2SO_4$  in each vessel was detd. The amt. of  $H_2SO_4$  formed in unit time is proportional to the square of the gross gas concn. or the square of the abs. pressure. The great effect of the concn. of  $NO_2$  is shown by the fact that increasing this from 0.5% to 2.46% raised the amt. of  $SO_2$  converted at the exit of the 4th vessel (there were 7 in all) from 6.72% to 94.42%, the compn. of the gas mixt. otherwise remaining the same. The reaction by which the  $H_2SO_4$  is formed in the chamber process is of the third order. The accelerating effect on the reaction rate of the surfaces of the contg. vessels is emphasized. F. C. Z.

**Studies on catalysts for the oxidation of ammonia.** I. KENKEI INABA. *Bull. Inst. Phys. Chem. Research (Japan)* **2**, 222-33(1923).—A mixt. of oxides of Fe and Bi was used as a catalyst for the oxidation of  $NH_3$ ; air was used as the source of  $O_2$ . When the ratio of the oxides of Fe and Bi was 67:33, the yield reached 85%; the temp. of the catalyzer was 750-800°, the layer of the catalyzer 0.5 cm., the content of  $NH_3$  about 8%, and the velocity of the gas about 1 l. per min. When the catalyzer was prepd. from  $Fe(NO_3)_3$  100,  $Bi(NO_3)_3$  20, and  $Th(NO_3)_3$  4 g., *i. e.*, it was a mixt. of oxides of Fe, Bi, and Th, the yield was increased. If the content of  $O_2$  in air is increased to 40% by mixing with  $O_2$ , the yield becomes 95%. For the prepn. of the catalyzer the nitrates were changed into hydroxides, dried at 140-80° and the portion passing sieves of 6-14 mesh per in. was roasted in a furnace. Oxides from other sources gave poorer yield. This catalyst must be used at a higher temp. than Pt and for a longer time.

K. KASHIMA

**Effect of dialysis on the direct crystallization of citric acid from lemon juice.** H. D. POORE. *Ind. Eng. Chem.* **15**, 775-8(1923).—Preliminary expts. with collodion sacs in dialyzing lemon juice, followed by dialysis on a large scale in an osmotic contg. cloth membranes impregnated with collodion, showed that (1) the small amt. of colloids present in lemon juice does not influence crystn., but the ash and the other non-acid

ingredients prevent satisfactory crystn. of concd. fermented juice; (2) in the presence of the ash and other impurities, needle and leaflet modifications of citric acid crystals are obtained and upon removal of 0.5 of the ash, characteristic crystals are formed; and (3) at the concn. necessary for crystn. the mother liquor is so viscous that the crystals cannot be sepd.

C. C. DAVIS

**Fifty-ninth annual report of the Alkali Inspector, 1922.** T. L. BAILEY. *Gas World* 79, No. 2033 (Coking Sec.), 14-7 (1923); *Gas J.* 163, 255-8.—Electrostatic deposition of dust is receiving considerable attention in  $H_2SO_4$  plants. At one contact plant, the exit gases are to be scrubbed with a soln. of  $Na_2CO_3$  with the production of bisulfite. In  $(NH_4)_2SO_4$  and gas liquor works the production of neutral sulfate is the outstanding feature. The Bedford process is assuming some importance in this respect (Hansford, *C. A.* 16, 483).  $NH_3$  products (expressed as sulfate 25.75%  $NH_3$ ) manufactured in Eng. and Wales amounted to 275,301 tons, of which gas-works supplied 144,817 and coke ovens 125,679 tons. In tar distn., the most recent innovation is the use of a molten lead bath for heat transference in the still. The tar is fed in below the surface. The total amt. of tar distd. in 1922 was 1,185,994 tons. Criticism is made that the consumption of lime and steam in the  $NH_3$  liquor stills shows too great variations and is greatly in excess of what is required. Discussion is given of the vol. and character of the effluent spent liquors to be treated and of their detn. (cf. Parrish, *C. A.* 16, 3759). The work begun last year (*C. A.* 17, 1109) on the decolorizing and dephenolating of the waste liquors by means of flue gases has been continued and further improvement made, although the % purification effected does not yet come up to expectations. In the final effluent discharged, analysis indicates a volatilization of 71% of the phenols with a reduction in the "O absorbed" of 42%. Further treatment of these liquors by bacterial action on specially prepared filter beds demonstrates that these liquors could be made practically innocuous in respect of phenol, thiocyanate and other oxidizable constituents. The pickling process in tinplate manuf. and the efficiency of various "restrainers" are discussed.

J. L. WILEY

**The causticizing of potash.** P. P. HUDNIKOV and I. K. SIRKIN. *Z. anorg. allgem. Chem.* 128, 131-6 (1923).—The causticizing of potash has not hitherto been investigated as fully as that of soda. To study this, varying amts. of  $CaO$  were stirred into solns. of  $K_2CO_3$  of various concns., at 20° and the  $OH$  and  $CO_3$  concns. in soln. were detd. after various time intervals. Equil. was attained within 48 hrs. (sooner at higher temps.). The equil. "constant"  $K = 2(OH)_2/2CO_3$  increases rapidly with diln. The yield of  $KOH$  at moderate concns. is 91-98%. At high concns. (from about 5 *N*) a double salt  $K_2CO_3 \cdot CaCO_3$  is deposited, in analogy to the case of  $Na_2CO_3$ , and the yield of  $KOH$  falls below 50%. An approx. phase diagram is given.  $SrO$  and  $BaO$  give higher yields than  $CaO$ , because of the greater soly. of their hydroxides and the absence of double carbonates.

R. S. MULLIKEN

**An untrodden field in lime research.** O. BOWLES. *Concrete* (Mill Section) 23, 127 (1923).—Limes vary greatly in their physical properties and chem. activities such as plasticity, rate of slaking, or rate of settling as milk of lime; these variations in many instances bear no relation to the chem. compn. of the original limestone. A definite relationship undoubtedly exists between the character of the lime and the physical properties of the parent limestone, but little serious effort has yet been made to correlate them.

J. C. WITT

**Chili nitrate and German nitrogen.** MARCEL POMIER-LAYRARGUES. *Prog. agr.* vit. 80, 57-60 (1923).—Discussion of trade conditions in these commodities.

P. R. D.

**A visit to the potassium mines of Alsace.** GINO CONTRI. *Rass. min. met. chim.* 58, 109-11 (1923).—The nature of the deposits, their historical development, recent improvements and industrial and agricultural value are described.

C. C. DAVIS

**German graphite.** E. H. SCHULTZ. *Glaser's Z.* 10, 155 (1923).—Historical and descriptive.

C. C. DAVIS

**Activated carbon—its evaluation, manufacture and uses.** FREDERICK BONNEY, JR. *Chem. Age* (N. Y.) 31, 327-31 (1923).

E. H.

**The fuller's earth industry.** A. BRITAIN. *Chem. Trade J.* 73, 93-5 (1923).—A review.

E. H.

**Bleaching of Gangwa wood (*Excoecaria agallocha*) in the manufacture of matches.** R. L. DATTA, T. ROSU and D. B. MEEK. *J. Indian Ind. Labour* 3, 38-45 (1923).—Expts. with various bleaching agents indicate that bleaching powder (0.25% available Cl in the bleaching soln.) gives the most satisfactory results in prepg. the dark colored Gangwa wood for match manuf. Methods of bleaching to be used on a factory scale are discussed.

LOUIS E. WISG

The potassium, bromine and iodine content of Black Sea alga (SHKATKLOV) 11D. The action of potassium carbonate on lead glass (RICHMOND) 19. Sodium sulfate (WELLS) 8.

**Nitric acid production by the electric arc.** W. SIEBERT. U. S. 1,462,052, July 17. See Can. 226,263 (*C. A.* 17, 693).

**Nitric acid production by the electric arc.** W. SIEBERT. U. S. 1,462,987, July 24. See Can. 228,883 (*C. A.* 17, 1694).

**Hydrocyanic acid.** M. E. MUELLER. Brit. 190,961, April 10, 1922. Hydrocyanic acid is recovered from gases contg.  $\text{NH}_3$ ,  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , by scrubbing with a Cu compd. such as  $\text{Cu}_2\text{S}$ ,  $\text{CuSO}_4$  or  $\text{CuO}$  in  $\text{H}_2\text{O}$ , the absorption being carried on until the soln. contains at least two atoms of Cu (as  $(\text{NH}_4)_2\text{Cu}(\text{CN})_4$ ) for each mol. of  $\text{H}_2\text{S}$  in soln. When starting with  $\text{Cu}_2\text{S}$ , therefore, no  $\text{H}_2\text{S}$  is absorbed. Alternatively less absorption may be effected and the soln. boiled to remove  $\text{H}_2\text{S}$  in excess, with the loss however of some HCN. In any case, a boiling is advantageous to remove  $\text{CO}_2$  and to avoid loss of HCN in this step it is preferred to add CuCN before the boiling, which causes the pptn. of  $\text{Cu}_2\text{S}$  (returned to the absorption step) and the formation of another cuprocyanide probably  $\text{NH}_4\text{Cu}(\text{CN})_2$ . The soln. is then distd. with dil.  $\text{H}_2\text{SO}_4$  to obtain HCN and insol. CuCN (and  $\text{Cu}_2\text{S}$  if the step of heating with  $\text{CuCy}_4$  has not been employed). The insol. matter may be returned to the absorption step. Cf. *C. A.* 16, 2202.

**Phosphoric acids; ferro-phosphorus.** H. G. C. FAIRWEATHER. Brit. 191,630, Feb. 1, 1922. Ortho-, pyro-, and meta-phosphoric acids are obtained by treating phosphatic material, coke and  $\text{SiO}_2$  with or without Fe, in an elec. furnace, oxidizing the liberated P in the furnace by admitting a regulated quantity of air, cooling the gases in a regulated manner, and sepg. the acid by an elec. precipitator or other means. When the gases are cooled to  $70\text{--}120^\circ$   $\text{H}_3\text{PO}_4$  of 70–80% strength is obtained, at  $120\text{--}210^\circ$   $\text{H}_3\text{PO}_4$  of 80–97%, at  $210\text{--}315^\circ$   $\text{H}_4\text{P}_2\text{O}_7$ , and at  $315\text{--}400^\circ$   $\text{HPO}_3$ . In each case the  $\text{H}_2\text{O}$  vapor is present in the gases cooled, being introduced in the oxidation air and as moisture in the charge, but additional  $\text{H}_2\text{O}$  may be introduced into the gases. A suitable construction is specified.

**Hydrating lime.** M. HERMANN. U. S. 1,462,284, July 17. Lump lime is subjected to a  $\text{H}_2\text{O}$  spray in a chamber through which it may be passed by a screw conveyor and is then allowed to fall on to a moving conveyor belt which permits evapn. and from which the product is collected in powdered form.

**Barium oxide.** W. VON DIETERICH. Brit. 191,215, Oct. 31, 1921. A mixt. of  $\text{BaCO}_3$  and a reducing agent such as C, pitch, tar, or the like is heated under reduced pressure in a rotary furnace or a furnace provided with means for agitating the reaction mixt. The furnace is preferably elec. heated internally, but heat may be applied instead, or in addn., from the outside.

**Ammonia recovery from gases.** INDUSTRIAL RESEARCH, LTD. Brit. 191,741, Jan. 10, 1923. To recover  $\text{NH}_3$  from producer gas, distn. gases and other gases contg. a small amt. of  $\text{NH}_3$ , the gas is passed through carbonaceous material contg. org. acids such as soft lignite or peat. The  $\text{NH}_3$  is liberated by means of alkali and the absorption material is regenerated by treating with an acid such as HCl and removing the excess acid. Alternatively the lignite, etc., after absorption of the  $\text{NH}_3$ , may be used as a fertilizer.

**Autoclave for ammonia synthesis.** E. H. ARNOLD and W. T. WAKEFORD. U. S. 1,463,280, July 31. Openings at the top and bottom of an autoclave with a metal shell are provided so that the charge can be removed from the autoclave by the combined influence of pressure and gravity.

**Nitrates, etc.** H. HAMPEL. U. S. 1,460,898, July 3.  $\text{KNO}_3$  and  $\text{CaSO}_4$  are formed by reaction of  $\text{Ca}(\text{NO}_3)_2$  on  $\text{K}_2\text{SO}_4$ . The  $\text{CaSO}_4$  is reacted upon by  $\text{NH}_3$  and  $\text{CO}_2$ , forming  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{CaCO}_3$  and the latter is then treated with  $\text{HNO}_3$  to regenerate  $\text{Ca}(\text{NO}_3)_2$ . Nitrates of Na or Mg may be similarly formed from their sulfates. *Iodides*, e. g.,  $\text{AlI}_3$  may be formed in a generally similar manner, by employing sulfates and using  $\text{CaI}_2$  and HI instead of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{HNO}_3$ . *Soda* is prepd. from NaCl by treatment with  $\text{Pb}(\text{OAc})_2$  and  $\text{PbCl}_2$  thus formed is treated with  $\text{NH}_3$  and  $\text{CO}_2$ , forming  $\text{PbCO}_3$ , which is treated with  $\text{HOAc}$  to regenerate  $\text{Pb}(\text{OAc})_2$ . If  $\text{H}_2\text{S}$  is used instead of  $\text{CO}_2$  in the latter process, the  $\text{PbS}$  formed is also similarly treated to regenerate  $\text{Pb}(\text{OAc})_2$ .  $\text{MgCl}_2$  is formed from  $\text{MgSO}_4$  by use of  $\text{CaCl}_2$ ,  $\text{NH}_3$  (or KOH),  $\text{CO}_2$  and HCl in successive reactions of the same type. Alkali metal chlorides also may be used as starting materials to produce nitrates. Cyclic processes of this kind may be operated with but little manufacturing losses.



**Alkali cyanides.** K. P. McELROY. Brit. 191,765, July 14, 1921. Cyanide-forming materials are fed to a chamber contg. cyanide, the necessary heat is supplied, part of the reaction gases is utilized to preheat the reaction materials, and the rest withdrawn through a side chamber contg. C maintained at a suitable temp. to prevent reversion, and the withdrawal of the cyanide from the reaction chamber is regulated so as to maintain a mass of cyanide therein. The reaction may be effected in a blast furnace or slagging gas-producer, the temp. at the reaction zone being maintained at 1200-1400° and the temp. of the side chamber at 1000°. The air is preheated, and the proportion between the gases passing up through the charge and the gases withdrawn through the side chamber is regulated so as to effect the conversion of all the alkali to cyanide. Alkali may be added to the C in the side chamber in the liquid state and C may be added in the side chamber in the form of hydrocarbons. Liquid cyanide is withdrawn from the side chamber. The alkali employed in the process is preferably used in the form of carbonate but sulfates, chlorides, silicates, or aluminates may also be used.

**Sodium tungstate.** BRITISH THOMSON-HOUSTON CO. LTD. Brit. 189,873, Sept. 8, 1921. For the production of Na tungstate from W ores in a continuous manner, a powd. mixt. of W ore,  $\text{Na}_2\text{CO}_3$ , and  $\text{NaNO}_3$  from a hopper is fed by a gate to a band conveyor supported by a shelf. A suitable construction is specified.

**Alkali metal silicates.** C. DEGUIDE. U. S. 1,463,037, July 24. See Brit. 174,581 (C. A. 16, 1838).

**Soluble compounds of potassium and aluminium from silicates.** B. F. HALVORSEN. U. S. 1,463,508, July 31. Silicates such as feldspar are heated with  $\text{CaCN}_2$  and  $\text{H}_2\text{O}$  to produce sol. compds. Chlorides, nitrates and sulfates may be added to facilitate the reaction.

**Water jacket for sodium silicate furnaces.** L. C. DREFAHL and W. R. CARSON. U. S. 1,463,204, July 31.

**Sodium decaborate.** A. A. KELLY. U. S. 1,462,004, July 17. B ore such as boronatrocalcite is treated with  $\text{H}_2\text{O}$ , heated and treated with  $\text{SO}_2$  to produce decaborate which seps. on cooling.

**Condenser for ammonia and carbon dioxide reaction products.** N. W. KRASE and V. L. GADU. U. S. 1,463,216, July 31.

**Phosphorus oxychloride.** R. L. ANDREAU. U. S. 1,462,732, July 24.  $\text{POCl}_3$  is prepd. by bringing phosgene into contact (at a temp. of 300-500°) with  $\text{FePO}_4$  or other phosphate which forms a chloride fusible at the reaction temp.

**Vanadium oxide catalyst.** H. D. GIBBS. U. S. 1,463,206, July 31. Infusorial earth is impregnated with molten  $\text{V}_2\text{O}_5$  to prep. a catalyst which is suitable for oxidation reactions. Cf. C. A. 17, 2631.

**Carbon catalyst.** C. B. JACOBS. U. S. 1,462,752, July 24. A C catalyst adapted for use in making  $\text{COCl}_2$ ,  $\text{CCl}_4$  or other products is prepd. by evapg. and calcining waste liquors of the *soda pulp* process. The product thus obtained becomes ignited in air at a temp. below 370° (sometimes even at 80-150°).

**Burners for producing lampblack.** J. L. DOSTAL. U. S. 1,462,691, July 24.

**Rendering artificial graphite impervious.** W. F. BLEECKER. U. S. 1,462,003, July 17. The surface of artificial graphite is coated with pitch or a similar material and volatile constituents are then evapg.

**Cement for radiators.** H. G. HALL. U. S. 1,462,747, July 24. A mixt. of portland cement 89, glue 4, rosin 1, lampblack 6 parts and sufficient  $\text{H}_2\text{O}$  to form a plastic mass is used for stopping leaks.

**Pitch-cement.** ICHITA KISHI. Japan. 42,291, Apr. 12, 1922. The cement is prepd. by melting a mixt. of the pitch of petroleum, coal, brown coal or peat and  $\text{MgO}$ .

**Plastic composition.** I. MANCHESTER. Brit. 191,421, Sept. 5, 1921. Granulated cork is mixed with 3-4 times its wt. of a vulcanizable rubber soln. contg. approx. 30% of rubber and is roughly shaped under a pressure which will approx. halve the thickness of the compn.—about 60-70 lbs. per sq. in. The article is removed from the mold, dried, and again subjected to pressure to reduce the vol. further, and vulcanized under pressure.

**Phenolic condensation products.** W. O. SNELLING. U. S. 1,462,771, July 24. An intermediate product is prepd. from a phenolic compd. and  $(\text{CH}_3)_3\text{N}$ , and a second intermediate product is also prepd. from a phenolic compd. and anhydrous polymerized formaldehyde. These two intermediates are then mixed in such proportions that the excess of  $\text{NH}_3$  in the first intermediate will balance the deficiency in the second intermediate.

**Adhesive paste.** B. L. PICKARD. U. S. 1,463,403, July 31. "Cactus liquid,"

2 gals., is mixed with glue 1 lb., corn starch 1 lb., shellac 1 qt. and alum 1 lb. to form a paste which may be used on wood, leather or woven fabrics.

**Waterproofing composition.** A. SCHMIDT. U. S. 1,462,381, July 17. A mixt. adapted for waterproofing wood or leather is formed of chlorinated Montan wax and turpentine, with or without lampblack, paraffin or other ingredients.

**Precooling air.** A. MESSER. U. S. 1,462,177, July 17. Air to be liquefied is pre-cooled by compressing the air, passing it in heat-exchanging relation with  $H_2O$  and cooling the  $H_2O$  by passing finely divided N or other dry gas through it.

**Multiply board.** W. STERICKER. U. S. 1,462,835, July 24. Plies of paper or similar material to be united are coated with a 34° Bé. soln. of Na silicate in which the proportion of  $Na_2O$  to  $SiO_2$  is 1 to 4 and the plies are united under pressure.

**Stationary chemical-mixing fire extinguisher system.** J. W. ENRIGHT. U. S. 1,463,072, July 24.

**Giving form to fuller's earth.** KIKUNAE IKEDA, HAJIME ISOBE and TSURUJI OKAZAWA. Japan. 42,368, Apr. 20, 1922. Short rough-surfaced cords or threads are made by pressing a mass which has been prepd. by kneading a mixt. of fuller's earth or Florida earth and 80-110% of  $H_2O$  through a small opening. They are then heated at 130-600°. These cords are used for drying air.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

**The fundamentals in the progress of the glass industry.** GUSTAV KEPPELER. *Z. Ver. deut. Ing.* 67, 509-12(1923).—A short history of recent technical advances in the glass industry. (Nonsol glass is credited as "English 1915" at which time it had a considerable sale there. This should have read "America, 1902".) G. E. BARTON

**A modern window-glass house.** R. KNORRN. *Z. Ver. deut. Ing.* 67, 513-6(1923).—A description of the recently completed plant of the Vereinigten Vopeliuschen und Wentzelschen Glashütten G. m. b. H. G. E. BARTON

**Glass furnaces.** H. MAURACH. *Z. Ver. deut. Ing.* 67, 517-22(1923); 11 cuts, 6 tables. G. E. BARTON

**Annealing glassware.** F. ECKERT. *Z. Ver. deut. Ing.* 67, 522-3(1923).

**The large-scale production of incandescent-lamp bulbs.** G. GEHLHOFF. *Z. Ver. deut. Ing.* 67, 524-6(1923). G. E. BARTON

**Lubrication of glass-making machinery.** ANON. *Glass Ind.* 4, 130-1(1923).

**Seeds in glass.** A. J. RITTMAN. *Glass Worker* 42, No. 42, 19, 20, 23(1923).—The remedy for seeds is almost invariably increased heat in the melting and refining. J. B. PATCH

**The staining and etching of glass.** L. SPRINGER. *Glashütte* 52, 289; 53, 277 (1922-3). J. B. PATCH

**Flattening stones.** C. J. STAHL. *Glashütte* 53, 307, 323-5, 339-41, 355-6(1923).—The mixing, shaping, firing and polishing are described. J. B. PATCH

**The electrodeposition of silver and copper on glass.** C. H. PROCTOR. *Glass Ind.* 4, 61-3(1923). J. B. PATCH

**Graphic check on glass-works operation.** WALTER J. KNOTHE. *Glass Ind.* 4, 83-5(1923). J. B. PATCH

**Avoiding errors in the analysis of glass sand.** J. B. KRAK. *Glass Ind.* 4, 103-4 (1923). J. B. PATCH

**The action of water and steam under pressure on some soda-lime-silicate glasses.** F. W. HODKIN and W. E. S. TURNER. *J. Soc. Glass Tech.* 6, 291-308(1922).—Four soda-lime-silicate glasses having the approx. compns.  $6SiO_2.0.3CaO.1.7Na_2O$ ,  $6SiO_2.0.7CaO.1.3Na_2O$ ,  $6SiO_2.0.8CaO.1.2Na_2O$ , and  $6SiO_2.CaO.Na_2O$  were subjected to the action of water and steam at pressures varying from 2 to 25 atms. above normal. The action of steam on these glasses is considerable, being greater than that of water at the higher pressures in the case of the glass having the lowest lime content. Corrosion diminishes as the amt. of lime is increased and the amt. of  $Na_2O$  decreased. The glass with the highest lime content was unattacked by steam or water in 3 hours at 2 to 4 atms. The incrustation formed as a result of corrosion was harder the greater the lime content; a gelatinous layer was formed beneath the incrustation on the glass contg. only

0.3CaO at 15 atm. pressure. Since the loss in weight recorded was less than the total alkali found in the water, it is clear that the glass absorbs a considerable quantity of water. The character of the corrosion, which clearly brings out pouring and molding lines, is influenced markedly by the condition of the surface. The autoclave test is considered too severe for soda-lime-silicate glasses which are only required to resist the action of boiling water.

**The action of potassium carbonate on lead glass.** H. D. RICHMOND. *Analyst* 48, 260-2 (1923).—A sample of  $K_2CO_3$  taken under the Sale of Food and Drugs Acts showed 10 parts of As and 80 parts of sol. Pb per million. Scrapings from the walls of the same bottle gave 12 pts. As and 500 pts. Pb per million. The bottles contained 0.21% of  $As_2O_3$  and 13.1% PbO. It was proved by expt. that  $K_2CO_3$  contg. 16.6% of moisture gave no increase of lead content in six weeks when kept in a "well closed lead glass bottle." A sample of  $K_2CO_3$  originally carrying less than 5 pts. per million of lead stored for 9 weeks in a lead-glass bottle with "very imperfect" closure contained 20.5% moisture and 150 pts. per million of lead at the end of the time. The result is attributed to the formation of a liquid phase on the surface of the crystals which acts on the bottles. It is recommended that  $K_2CO_3$  be not stored in lead-glass bottles.

J. C. S.

**The cutting and polishing of mirror glass.** ADOLF SCHILD. *Z. ver. deut. Ing.* 67, 538-43 (1923); 19 fig.

G. E. BARTON

**The diphasic nature of glass, as shown by photo-elastic observations.** L. N. G. FILON AND F. C. HARRIS. *Proc. Roy. Soc. (London)* 103A, 561-71 (1923); 3 figs., 2 tables.—A specimen of flint glass was heated slowly to 400° and then subjected to a longitudinal pressure of 130.6 bars. The full load was left on for 42 hrs. and then the specimen was allowed to cool slowly under this pressure; the process took 7 hrs. The load was removed and the specimen examd. in Na light between crossed Nicols with the aid of a Babinet compensator. The black band indicated a stress difference which was quite considerable and remained of the same sign throughout a cross-section of the specimen. This band extended up to the edge, excluding a possible "skin effect" as the source of a balancing stress. The conclusion, after a mathematical analysis of the results, is "that a portion of the stress is not optically shown. It necessarily follows that the material cannot be homogeneous, but must consist of at least 2 components or 'phases'." "Further these phases must have different stress-optical coefficients." The stress-optical coeff. for the heavy flint glass in question only changed from 2.31 brewsters to 2.24 brewsters during the above treatment. "It would thus appear that the heat treatment has produced practically no change in the constn. of the disperse phase, so that the phases have not sepd. out, but have been present in the glass from the beginning." An extra-dense flint examd. in the same manner gave positive values for the longitudinal stress, whereas these values were negative in the case of the heavy flint glass. From the above fact, the conclusion is that the "crypto-stress" is an effective pressure in the case of the extra-dense flint. It is suggested that according to Wieners' hypothesis if the particles of the disperse phase are small compared with the wave length of light, the double refraction due to stress would be largely influenced by change of shape and orientation of the dispersed particles. Further expts. are in progress.

G. E. BARTON

**Adsorbent properties of clay.** M. A. RAKUSIN. *Chem.-Ztg.* 47, 115 (1923).—Ordinary clay, especially when ignited, possesses adsorbent properties similar to those of kaolin. A 1% soln. of petroleum in petroleum spirit, colored a deep reddish brown, was completely decolorized by standing for 24 hrs. in contact with 5% of ignited clay or 8% of air-dried clay. Suspensions of indigo in aromatic hydrocarbons were colored yellow after this treatment, while suspensions of indigo in petroleum spirit, kerosene, and vaseline oil were colorless. Aromatic hydrocarbons extd. from air-dried clay a yellow oil, insol. in petroleum hydrocarbons. This oil is probably derived from straw and manure kneaded into the clay during its prepn.

J. S. C. I.

**Studies on clays. I. The acidic reaction of Japanese acid clays.** TSURUJI OKAZAWA. *Bull. Inst. Phys. Chem. Research (Japan)* 2, 189-221 (1923).—K. Kobayashi has attributed the acidity of Japanese acid clay to its adsorptive action. O. has proposed a different explanation. Clays have many varied appearances and properties, but may be classified into 3 kinds from their reactivity to salt solns. and acids. When treated with salt solns. or strong acids, the first shows little or no soly, the second none for salt solns. but high with acids, and the third shows high soly. with both. Japanese acid clay belongs to the last class, but is not very different in compn. from common clays. When treated with salt solns., the positive radical in the neutral salt is drawn into the clay particle and Al in the latter is dissolved as a corresponding salt; e. g.,

when  $MgCl_2$  is used as the neutral salt, the reaction may be as follows:  $R: Al(OH) + MgCl_2 = R:Mg + AlCl_3OH$  and  $AlCl_3OH + 2H_2O = Al(OH)_3 + 2HCl$ , where  $R$  is the main radical in the clay;  $HCl$  thus produced gives the acidic reaction. This reaction is, therefore, considered to be attributed partly to adsorption and mainly to double decompn. and the acidity is governed by the salt used, adsorptive and reactive affinities of the clay, stability of the reaction product and reaction velocity, etc. The value of the acidity is not definitely detd. by titrating with alkali. The so-called acidity of the acid clay is decreased greatly by burning at  $700-800^\circ$  for 1 hr. By heating, the state of mol. combination will be changed and  $Al_2O_3$  in the clay will not be dissolved by salt solns. The relation between the burning and the quantity of  $Al_2O_3$  dissolved from the clay by acid is opposite to the above relation. The higher the temp of burning, the more  $Al_2O_3$  is dissolved, the max. being at about  $700-800^\circ$ ; the quantity dissolved is larger than that of other clay. At above  $900^\circ$  the quantity decreases quickly.

K. KASHIMA

**Action of heat on kaolins, clays, etc.** A. BIGOR. *Compt. rend.* 176, 91-3 (1923).—The materials were dried, ground and passed through a silk bolter No. 200. From each clay thus prepd. 2 series of test pieces were made, the first of soft paste, the second of powder with 4-8%  $H_2O$  compressed by 375-400 kg. sq. cm. The test pieces were heated to from  $400^\circ$  to  $1000^\circ$  and any changes noted. Plastic ceramic materials, when heated, first harden without dehydration or contraction in vol., this hardening resulting from the partial pectization of the colloids which they contain. After dehydration and above  $700^\circ$ , heat produces a phys. transformation accompanied by contraction and the material continues to harden, at the same time the colloids disappear. Non-plastic ceramic material hardens only at about  $1000^\circ$  after complete dehydration, which takes place at between  $650^\circ$  and  $700^\circ$ . The pectization of the colloids plays an important role in the ceramic and terra cotta industries. **Black potteries.** *Ibid.* 510-3.—Black pottery includes (1) those which through firing have lost their combined  $H_2O$  (cf. LeChatelier, *Compt. rend.* 121, 386) and (2) those which have held their combined  $H_2O$  and which consequently have been fired at a temp below  $600^\circ$ . The 2nd group forms the object of this study. Samples of very old Etruscan pottery were analyzed and were ground to an impalpable powder from which test pieces were prepd. From the tests it is concluded that the manu. of non-dehydrated black pottery is based on the phenomenon of the partial pectization of the colloids of the clay. **Colloidal plasticity.** *Ibid.* 1470-3.—Partial pectization of the colloids of clays takes place at  $350-600^\circ$ . On heating from  $600^\circ$  to  $1000^\circ$ , the combined  $H_2O$  is driven off between  $600^\circ$  and  $700^\circ$  and the pectization appears complete. Clays and kaolins heated to  $1000^\circ$  then ground to an impalpable powder and mixed with  $H_2O$ , do not regain plasticity. These mixts. after heating at  $500^\circ$  for 4 hrs. slake immediately when plunged into  $H_2O$  after cooling. Clays from the region of Chauny were subjected to porosity, molding and other phys. tests to det. their fitness for making building brick.

L. W. RIGGS

**Experiments on the low-temperature final firing of porcelain.** W. FUNK. *Sprechsal* 55, 312-3; *Chem. Zentr.* IV, 700-1, 1922.—The expts. were carried out at cones 8-9 in the compn. range specified by Hertwig-Möhrenbach. In general the stability of the porcelains was not great.

C. C. DAVIS

**Use of the filter-press in preparing the body for stanniferous faience.** V. LUCAS. *Rev. Mat. Constr. Trav. Pub.* 163, 74B-75B (1923).—Good results are claimed to be obtained by mixing and grinding the raw materials, clays, marls and grog (at least  $1/4$  of the total), then working them up in a blunger, passing the mixt. through a rocking screen into an agitator, then through a filter press. The importance of the initial fine grinding and the addn. of sufficient quantities of antiplastic material is emphasized.

LOUIS NAVIAS

**The effect of nickel salts on the color [of glazes].** G. M. TUCKER. *New Jersey Ceramicist* 4, 268 (1921).—Four calcines were prepd. as follows: *A*, salt 20, flint 80; *B*, salt 16.7,  $ZnO$  41.7, flint 41.67; *C*, salt 16.7, whiting 41.7, flint 41.6; *D*, salt 16.7,  $MgO$  41.7, flint 41.7. In each of the calcines various  $Ni$  compds. were substituted successively for the salt. The calcines were ground dry and burned to cone  $5\frac{1}{2}$  in a commercial terra cotta kiln, reground and washed. Five % of each calcine was substituted successively in each of two glazes. One glaze contd. Cornwall stone, a high %  $CaO$  and no  $ZnO$ . The other was of the Bristol type. Colors obtained varied through a considerable range, which is given in detail.  $MgO$  in calcine *D* exerted a greater influence on color than the  $Ni$  itself when used in the Bristol glaze.

C. W. PARMELER

**Slip glazed ware.** ANT. HÜTTL. *Keram. Rundschau* 31, 89 (1923).—Brown ware is made in many portions of Germany. The appearance varies in different localities, depending upon the nature of raw materials. Many clays can be used in their natural

state to produce glazes if fired sufficiently high but fluxes are usually added to reduce their maturing temp. The analysis of a slip glaze is as follows:  $\text{SiO}_2$  59.10,  $\text{Al}_2\text{O}_3$  11.72,  $\text{Fe}_2\text{O}_3$  4.16,  $\text{CaO}$  7.46,  $\text{MgO}$  1.84,  $\text{K}_2\text{O}$  4.85,  $\text{CO}_2$  6.09 and loss on ignition 4.80%; this corresponds to the following formula:  $10.04 \text{ SiO}_2$ ,  $0.136 \text{ Al}_2\text{O}_3$ ,  $0.029 \text{ FeO}$ ,  $0.095 \text{ CaO}$ ,  $0.049 \text{ MgO}$ ,  $0.051 \text{ K}_2\text{O}$ . Slip glazes are cheaper than artificial glazes. The Na in wood ashes is often dissolved in  $\text{H}_2\text{O}$  and this soln. mixed with the glaze. The Na lowers the maturing temp. and improves the quality of the glaze. H. G. SCHURECHT

**Some notes on materials and processes in electrical porcelain manufacture.** T. A. KLINEFELTER. *New Jersey Ceramist* 1, No. 4 (1921). C. W. PARMELEE

**The production of porcelain for electrical insulation.** III. F. H. RIDDLE. *J. Am. Inst. Elec. Eng.* 42, 631-5 (1923); cf. *C. A.* 17, 2483.—China and ball clays are tested for fired color, porosity, fineness of grain, and strength. Particular emphasis is placed upon the grain size of quartz, for which water sepn. is recommended. Limits of compn. are wide but the quality depends on the compn. Special spark-plug porcelains are made by eliminating feldspar and quartz and substituting synthetic calcines. Firing first drives out the  $\text{H}_2\text{O}$  then the feldspar melts and dissolves the clay and quartz or assists these to change into sillimanite and free  $\text{SiO}_2$ . The soln. of quartz depends upon the grain size and heat treatment. Ordinary porcelain has a tensile strength of 3000-6000 lbs. per sq. in. and a coeff. of linear expansion of  $4-9 \times 10^{-6}$  per  $^\circ$ , while special porcelain may reach a strength of 12000 lbs. and a coeff. of  $2.7 \times 10^{-6}$ .

W. E. RUDER

**Correct notions on fluoride enamels.** CHARLES MUSTOL. *Chimie et industrie* 9, 872-87 (1923).—A mathematical criticism of the theories of Vogt, Gruenwald, and Mayer and Hayas (*Sprechsaal* 1911, No. 1), based on the analyses published by these authors. It is shown that F is not volatilized as  $\text{SiF}_4$ , that when  $\text{B}_2\text{O}_3$  is present F is probably volatilized as  $\text{BF}_3$  (this would require to be confirmed by analysis of the gases evolved), and that Mayer and Hayas' results abound in errors, either clerical or analytical. A method is given for calcg. the compn. of the enamel from that of the initial mixt. Seger's formula is worse than useless. The relationship between the various constituents should be studied by means of the centesimal mol. compn. A. PATINEAU-COUTURE

**The influence of fluxes on the transformations of quartz.** N. PARRAVANO AND C. ROSSELLI DEL TERCO. *Gazz. chim. ital.* 53, 249-57 (1923).—In previous work P. (*Ann. chim. appl.* 10, 150 (1918)) clarified the nature of the transformations that take place in the burning of  $\text{SiO}_2$  refractories, which consists substantially in converting quartzite into varieties having a greater vol., i. e., tridymite, and cristobalite. This transformation occurs with or without the aid of the flux formed from the natural impurities present in the quartzite and of the lime used. After reviewing the existing information P. and T. describe their own expts. in which a quartzite ( $\text{SiO}_2$  96.5,  $\text{Al}_2\text{O}_3$  2.06,  $\text{CaO}$  0.80%,  $\text{Fe}_2\text{O}_3$  trace) was used to which 0.5, 1.0 and 1.5% oxides were added ( $\text{Fe}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{WO}_3$ ). The bricks were heated first 12 days at cone 15 ( $1430^\circ$ ) and then again for 15 days at cone 18 ( $1490^\circ$ ). The d. was detd. on the finely ground product. Microscopic examn. as well as the d. detns. showed under the conditions used, of which the absence of alkali was the most interesting, that  $\text{B}_2\text{O}_3$  has the greatest accelerative action on the transformations of quartz even when only 0.5% is present. Its catalytic activity is so energetic that in practice it ought to be suitably weakened in order to be used advantageously.  $\text{Fe}_2\text{O}_3$  has a notable catalytic action, perhaps through the formation of silico-ferrites as well as silico-aluminates (from the  $\text{Al}_2\text{O}_3$  always present) giving mixts. fusible at temps. not too high. In this case the d. does not reveal the phenomena as well as the microscopic observations. E. J. WITZEMANN

**Silica in Canada—its occurrence, exploitation and uses.** I. Eastern Canada. L. H. COLE. Can. Dept. Mines, *Mines Branch* No. 555, 126 pp. (1923). E. H.

**Rammed linings replace bricks.** AXON. *Brit. Clayworker* 32, 17 (1923).—Owing to the high price of fire brick, the use of rammed lining of ganister or silica rock is becoming popular. Steel furnaces, cupolas used in foundries, calcining furnaces, lime kilns, vertical cement kilns, and many reverberatory furnaces may use rammed linings. About 20,000 tons per mo. of ganister are used in Germany in this way. An almost pure  $\text{SiO}_2$  rock is crushed to powder, mixed with about 2%  $\text{CaO}$ , and then ground into a stiff paste with  $\text{H}_2\text{O}$ . The furnace is fitted with adjustable lining rings or with blocks, which are placed so as to act as one side of a mold, while the furnace wall acts as the other side. The experience of 4 yrs. has shown the process to be highly economical. Patching is done after every heat, and a relining is not necessary for 2 or more yrs.

H. G. SCHURECHT

**Making stiff mud fire brick.** A. D. COCHRAN. *Brick and Clay Record* 62, 852-4 (1923).—Grind the plastic clay as fine as possible; do not grind the flint clay and cal-

cined clay too fine (general practice is to pass through a screen from  $\frac{3}{16}$  to  $\frac{1}{16}$  inch); weathering the clay greatly improves it; addn. of calcined clay greatly reduces spalling (each 1% of calcined clay added will reduce spalling about  $\frac{5}{16}$ ); temper the clay thoroughly; keep moisture to a max. rather than down to the min.; cut brick as close to the die as is possible; use a good grade of brick oil on the cutter and represses, as excessive quantities of oil will cause the brick to crack; avoid die cracks in the clay bar (while cracks will close in repressing they will open again in drying and burning).

J. W. HEPPLEWHITE

**Carbonized bricks.** W. SMITH. *Brit. Clayworker* 32, 17(1923).—Carbonized bricks are produced by treating clay with C-charged gases; they are different from brick made with a mixt. of C and clay. Carbonized clay is of 2 kinds, black and white; the former is adapted for heat resistance in reducing atm., while the latter should be used in an oxidizing atm. As a heat conductor, the clay should be used in the black condition, as a nonconductor, in the white. Carbonized clay is recommended for filter beds, and the production of high-class acid-resisting ware; its hardness is just short of that of SiC. The carbonized brick conducts twice as well as standard firebrick. Attention is drawn to the possibility of liberating  $\text{Fe}_2\text{O}_3$  from red clays by this process. Alkalies may also be liberated.

H. G. SCHURECHT

**Keramite bricks.** ANON. *Süddeutsche Tonind.; Brit. Clayworker* 32, 17 8 (1923).—Keramite bricks are very hard and strong. The body consists of a well ground clay and quartz sand, or some similar material. The clay serves as a bonding and sintering medium, while the sand raises the m. p. Clay and sand are mixed together dry and 6–8%  $\text{H}_2\text{O}$  is added for dry pressing at 250 atm. Firing is at cone 13. In Hungary, Keramite brick has long been used as a paving material. Compressive strength is 64,000 lbs./sq. in. Analysis is 54  $\text{SiO}_2$ , 14  $\text{Al}_2\text{O}_3$ , 8  $\text{Fe}_2\text{O}_3$ , 16 CaO and 4–5  $\text{MgO}$ . On account of the high CaO content the Budapest brick are yellowish green in color.

H. G. SCHURECHT

**Fire-brick disintegration.** C. E. NESBIT and M. L. BELL. *Brick and Clay Record* 62, 1042–3(1923).—Fire-brick disintegration in linings of blast furnaces seems greatest 40 to 50 ft. from the top of the furnace. Disintegration is attributed to objectionable Fe compds. The CO in the furnace atm. reacts with  $\text{Fe}_2\text{O}_3$ , depositing voluminous graphitic C, which bursts the brick. The reaction is fairly rapid at 325° to 525°. Brick contg.  $1\frac{1}{2}\%$  FeS, failed in practically the same manner as brick with a corresponding amt. of Fe ore. The only practical remedy is to weather the clays in a layer not over 2 ft. thick for at least 2 mo. If the weather is dry, the layer must be watered weekly. This treatment will oxidize the Fe compds., which will be apparent by a change to a brown or yellow color. Such lumps or patches must be discarded and only the unstained clay used. Should the clay slake or break up readily, it should be turned over with a plow or some mechanical means to expose the under side and the sorting repeated after weathering.

J. W. HEPPLEWHITE

Lignite gas and its use in the ceramic industry (FABER) 21. Scale of hardness for glass and crystals (HAILLÉ) 2.

**Optical glass.** GENZO SHIMAZU. Japan. 43,203, August 1, 1922. Oxides of Pb are prepd. by oxidizing Pb powder by means of natural oxidation or other methods without melting. They are used in batches for optical glass together with  $\text{SiO}_2$ ,  $\text{Na}_2\text{CO}_3$ , CaO and other usual raw materials.

**Improvement in borosilicate glass.** KITSUZO FUHA. Japan. 42,161, Mar. 31, 1922. The new glasses has the following compn.:  $\text{SiO}_2$  66.0–67.5,  $\text{Al}_2\text{O}_3$  1.0–1.75,  $\text{Na}_2\text{O}$  7.0–8.0 and  $\text{B}_2\text{O}_3$  22.0–24.0%. The glass adheres more air-tightly to W wire and resists changes of temp. and weathering better than present borosilicate glasses.

**Glass furnace.** SADAJIRO KONO. Japan. 41,629, Jan. 31, 1922. Addn. to 35,150. A small furnace fixed to the main one for holding clear melted glass has a delivery orifice in the bottom, in which a rod rests. By the piston-like motion of the rod, a definite quantity of melted glass is pushed away from the orifice, and is received in a mold of a suitable form.

**Porcelain.** C. C. TREISCHEL. U. S. 1,462,396, July 17. See Can. 220,737(C. A. 16, 2973).

**Decorating pottery.** KOSABURO KANO. Japan. 38,872, June 11, 1921. A design or lettering is printed on paper with a paste composed of glaze 8, orchid-root 1, sirup, sugar or rice-jelly 1 and the proper amt. of warm  $\text{H}_2\text{O}$ ; then it is transferred on bisected ware. A hard fire color is painted on and around the design or lettering. The print repels the color and remains uncolored. The glaze is applied on the whole surface and the ware is fired at high temps.

**Rough-surfaced architectural pottery.** ICHIRO YOKOI. Japan. 43,328, Aug. 23, 1922. Green bodies made of feldspar, granite and bog Fe ore are put in a sagger, with small spaces between them. The sagger is then filled with powd. calcined quartz. By firing it to a temp. a little below the m. p. of the body mottled wares with rough surface are obtained.

**Roofing-tile kiln.** TATSUJIRO KISHIMOTO. Japan. 43,050, July 11, 1922. A roofing-tile kiln has 3 chambers arranged so as to form an arch, the middle chamber being built over the passage between the other 2. The waste gases of the lower chambers are made to pass through the middle one.

**Refractory products from dolomite.** C. A. LONGBOTTOM and F. L. DUFFIELD. U. S. 1,463,399, July 31. Binding materials such as clay and slag or Fe oxide are mixed with raw dolomite, molded articles are formed from the mixt. and subjected to an intense shrinking heating and are then dipped in a sealing material such as wax or tallow.

**Dolomite refractories.** C. A. LONGBOTTOM, F. L. DUFFIELD and W. J. REES. Brit. 191,412, July 4, 1921. Refractory products composed of dolomite are sealed against hydration after firing by immersion in molten wax, tallow, dehydrated oils or fats, or similar substances. Clay and either  $\text{Fe}_2\text{O}_3$  or slag may be added to the dolomite in the preferred proportions of 2-10% of  $\text{Fe}_2\text{O}_3$  and 2-15% of clay, or 2-10% each of slag and clay. The mixt. is molded into bricks and shrunk by heating to about  $1600^\circ$ .

**Abrasive mixture for fitting pistons in cylinders.** C. C. BUTTONFIELD. U. S. 1,463,501, July 31. Alundum 27,  $\text{PbCO}_3$  32 and graphite 41 parts. U. S. 1,463,502 specifies a mixt. of  $\text{PbCO}_3$  with about three times as much  $\text{SiO}_2$ , of which 5% is 40 mesh, 5% 60 mesh, 15% 80 mesh, 50% 100 mesh and 25% 200 mesh. A small amt. of graphite also may be added to this mixt.

## 20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

**Free lime in a portland cement clinker.** H. PASSOW. *Zement* 12, 143-5(1923).—Quartz sand acts as an inert material when mixed with a portland cement clinker. Blast-furnace slag when mixed with the clinker causes an increase in the amt. of free lime formed during the initial hardening.

R. F. SCHNEIDER

**Free calcium hydroxide in hardened portland cement.** GOSLICH. *Zement* 12, 149-50(1923).—A sample of hardened portland cement was exposed to moist air for 6 days. It was then dried at  $90^\circ$  and ground to a fine powder. The sample was fractionated by a suspension analysis into the following portions: 1.78% heavier than 2.84 (sp. gr.); 40.72% between 2.84 and 2.7; 25.25% between 2.7 and 2.6; 16.53% between 2.6 and 2.44; 7.81% between 2.44 and 2.23; and 7.93% lighter than 2.23. This latter portion should contain all the free  $\text{Ca}(\text{OH})_2$ , since  $\text{Ca}(\text{OH})_2$  itself has a sp. gr. of 2.078. The analyses of the fractions show that the lighter portion contains 12% excess  $\text{CaO}$ . This represents 0.95% of the total cement and indicates that free  $\text{CaO}$  is not formed during the hardening period.

R. F. SCHNEIDER

**How much water is chemically combined in a hardened portland cement?** GOSLICH. *Zement* 12, 163-5(1923).—Test specimens were made with 100 g. cement and 26 g. distd. water. These were stored in a moist closet. Samples were analyzed at various intervals from 1 hr. to 28 days after the mixing with water. The combined water was detd. as follows: The samples were powdered and dried to const. wt. at  $90-5^\circ$ . Two g. were ignited to const. wt. The loss in wt. minus the loss due to the volatile matter as previously detd. is the chemically combined water. In one cement 1.63%  $\text{H}_2\text{O}$  had combined at the end of the first hr. The amt. combined gradually increased to 13.36% at the end of 28 days.

R. F. SCHNEIDER

**The water content of mixtures for reinforced concrete.** L. SANTARELLA. *Ingegneria* 1, 93-5(1923); *Chimie et industrie* 9, 1187(1923).—A low water content increases the elasticity and resistance of the cement and decreases the deformation, and appreciably increases its adherence to the Fe. When the vol. of water passes from 15 to 12.5% there is a slight increase in adherence; but when it passes from 12.5 to 10% the adherence increases as much as 60%.

A. PAFINRAU-COUTURE

**The manufacture of portland cement from marl.** R. E. KIRK. Univ. Minn. Eng. Expt. Sta., *Bull.* 2, 53 pp.(1923).—Portland cement can be made from marl and clay, of as good a quality as that made from any other raw materials. The origin of marl, its chem. compn., and the quality and quantity available in Minnesota are discussed. Plant operations are taken up in detail.

R. F. SCHNEIDER

**The properties of portland cement.** H. BURCHARTZ. *Zement* 12, 186-7, 193-5

(1923).—A tabulation and discussion of the results of physical tests on 110 samples of port. cement. R. F. SCHNEIDER

Trass in a mixture with portland cement. GOSLICH. *Zement* 12, 145-6(1923).—Trass mixts. are difficult to prep. and handle. A concrete made with a good gravel will give equally satisfactory results. R. F. SCHNEIDER

The action of trass in a mixture with portland cement. HERRMANN. *Zement* 12, 179-81(1923).—Hardened portland cement (1) reacts alk. to phenolphthalein, (2) absorbs  $\text{CO}_2$  and forms  $\text{CaCO}_3$ , (3) reacts with soaps and fats to form Ca soaps, (4) reacts with fluorides, fluosilicates and silicic acid, (5) reacts with metal salts to form their hydroxides, (6) forms Ca thioaluminate, (7) requires a large amt. of acid to neutralize 1 g. of cement when suspended in water, (8) attacks metallic zinc and lead, (9) has a marked increase in elec. cond. over non-hardened port. cement, and (10) has definite microscopic properties. These properties show that free CaO and  $\text{Ca(OH)}_2$  are present in portland cement. Trass increases the CaO and  $\text{Ca(OH)}_2$ , when mixed with portland cement and also increases the strength. R. F. SCHNEIDER

Determination of the suitable fineness of grinding of materials used in the manufacture of cement. F. TIPPMANN. *Zement* 11, 541(1922); *Chimie et industrie* 9, 1187(1923).—Blast 3-4 g. of the material for 10 min. in an old Pt crucible so as to form a completely fused clinker which is evenly colored a blackish green after cooling. Brown, yellow, or even white spots, observable with a magnifying glass, clearly indicate that the material was not ground sufficiently fine. If the temp. is raised above the softening point there are formed fissures having a whitish green color, which might lead to false conclusions. A. PAPINEAU-COUTURE

The fine grinding of cement raw mix. F. TIPPMANN. *Zement* 12, 150-1(1923); cf. C. A. 17, 2484.—Extreme fineness is not necessary for cement raw mix, provided the clinker is thoroughly sintered. R. F. SCHNEIDER

Fineness of raw mix, strength, and impact test. H. KUHLE. *Zement* 12, 155-8, 174-7(1923).—A review and discussion with a bibliography. R. F. SCHNEIDER

A new application of the electric furnace. Fused aluminous cement. A. BRISSAUD. *Science et industrie* 6, 83-6(1922); *Chimie et industrie* 9, 1187(1923).—A description of the manuf. of fused aluminous cement in the elec. furnace. Furnaces of 1,000-2,000 h. p. are used, giving 25-40 tons a day. The cement is tapped every 3-4 hr. Power consumption is 1,000-1,400 kw. hr. per ton. There is considerable wear of the electrodes, owing to the action of the  $\text{CO}_2$  from the limestone, atm. O, and oxides, and mechanical abrasion during charging. (Cf. J. Bied, C. A. 15, 583; E. Candlot, C. A. 16, 1845.) A. PAPINEAU-COUTURE

The possibilities of manufacturing portland cement in the United Provinces. E. R. WATSON, K. C. MUKERJEE and N. G. CHATTERJEE. *Bull. Indian Ind. Labour* 30, 41 pp.(1923).—The availability of raw materials, fuel and sources of power for the manuf. of portland cement in India are discussed. Present economic conditions in India justify the construction of additional cement plants. R. F. SCHNEIDER

British Columbia plant contains unique features. H. ANDERSON. *Concrete (Mill Section)* 23, 113-5(1923).—An account of the Bamberton plant of the British Columbia Cement Company, Ltd. The raw materials, manuf. process, and equipment are discussed. J. C. WITT

Acid-proof cements. ANON. *Chem.-Ztg.* 47, 504(1923).—Water glass is a component of practically all acid-proof cements. Complete drying out and a thorough fixing of the cement after drying are essential. Usually this fixing is carried out with a dil. acid applied in repeated coats. Alkalies are harmful to these cements, and no cement is known equally resistant to both acids and alkalies. W. C. BRAUGH

Manufacture and application of lightweight concrete slabs. A. G. WIKOFF. *Chem. Met. Eng.* 28, 975-6(1923).—A mortar is made with 3 parts of cement, 1 of sand and 7 of a material which is solid at ordinary temp. but melts in hot water. This latter material is formed into pellets before mixing with the cement and sand. The mortar is molded into slabs which are reinforced and allowed to set. After setting the pellet material is removed by heating and steam-distg. The slabs are  $24 \times 32 \times 1\frac{1}{4}$  in. and weigh 30 lb. They are porous, strong, and resistant to the effects of heat and steam. R. F. SCHNEIDER

The protection of concrete and other building materials against water and noxious fumes. M. TOCH. *Ind. Eng. Chem.* 15, 665-6(1923).—A general discussion of the protection of concrete, steel and wood in buildings. R. F. SCHNEIDER

Corrosion of iron in concrete. B. ZSCHÖKKE. *Concrete Constr. Eng.* 18, 393-4(1923).—A summary of a report of the Zurich Institute for Testing Materials. A compact concrete in sufficient thickness will protect iron against oxidation for a consider-



able time provided shrinkage cracks do not reach the iron. A coating of red lead will prevent iron from rusting for 5 years. The problem of prevention of shrinkage cracks has not been solved. These cracks appear in rich concrete oftener than in lean concrete. The inhibitive action of chromates is being studied but conclusive results have not been obtained. The following precautions for preventing the corrosion of iron in concrete are recommended: (1) The concrete should not be too meager, but should contain the best percentage of cement so as to make it impermeable to air. Thus, the proportion of  $\text{Ca}(\text{OH})_2$ , which prevents oxidation, is increased, and the concrete is also more permeable to  $\text{CO}_2$ , which neutralizes the lime. (2) There must be no substances in the concrete such as locomotive cinders, often contg. S, which exert a chemical action on iron. (3) The layer of concrete covering the iron should be of sufficient thickness properly to cover it, and should not crack under pressure or through shrinkage.

J. C. WITT

**Plaster of Paris technology—effect of heat on gypsum.** C. ELLIOTT. *Chem. Trade J.* **72**, 725-6(1923).—The first effect of heat on gypsum is to change the crystals from the monoclinic to the orthorhombic form without the loss of water. Further heating liberates the water of crystn. E. discusses in detail the methods used in the different countries for the manuf. of plaster of Paris.

R. F. SCHNEIDER

**Cresote shortage tends to curtail preservation of wood.** C. M. TAYLOR. *Railway Engineering Maintenance* **19**, 159(1923).—Mixing crude oil with cresote on 50-50 basis will conserve supply and afford adequate protection.

R. C. BARDWELL

Burning pulverized fuel with cement as a by-product (Japan. pat. 43,420) 21.

**Paint for waterproofing cement.** NAKAJIRO MANO and RYUJIRO YANAKA. Japan. 42,350, Apr. 18, 1922. Fatty acid and solid paraffin are dissolved in naphtha of low m. p.

**Treating dust from cement kilns.** D. S. JACOBUS. U. S. 1,463,363, July 31. A flue with refractory heated side walls carries dust-laden cement-kiln gases past baffles which direct the gas and dust to the heated side walls to form a caking material. The side walls are accessible for cleaning while the app. is in operation.

**Plaster of Paris.** SEIKICHI FUKUZAWA, ITO FUKUZAWA and TOYO GIPS CO. Japan. 43,679, Oct. 11, 1922. The product of chem. reaction between  $\text{H}_2\text{SO}_4$  and  $\text{CaO}$  is left in a heap until the grains acquire a spheroidal shape. They are then washed with  $\text{H}_2\text{O}$  to get rid of  $\text{MgSO}_4$ . They are again left in a heap until the spheroidal shape of grains is formed. They are then used in the manuf. of plaster of Paris.

**Building block of ferro-manganese slag.** R. L. TAYLOR. U. S. 1,462,991, July 24. Ferro-Mn slag is crushed, mixed with  $\text{H}_2\text{O}$  to form a plastic mass, molded under pressure, treated with steam and dried.

**Artificial stone.** TOYOJI HATANAKA. Japan. 42,502, May 8, 1922. A white powder consisting of  $\text{MgO}$ ,  $\text{ZnO}$ , ground glass or other mineral substance, white Portland cement and clay, and a soln. of  $\text{MgCl}_2$ , *Gloiopeltis furcata* (a kind of glue) and alum in  $\text{H}_2\text{O}$  are used in making artificial stones.  $\text{MgCl}_2$  is sometimes omitted from the soln.

**Paving material.** KOMAKICHI KATO and CHIAKI KAMIBAYASHI. Japan. 42,701, May 30, 1922. Ground soy bean is treated with a soln. of an alkali. Any sol. Al salt and coal dust are added. The mixt. is used in paving together with cement, lime, sand, etc.

**Composition flooring.** W. H. H. NORRIS. Brit. 191,315, March 11, 1922. Flooring, etc., composed of a mixt. of wood meal, magnesite, and  $\text{MgCl}_2$  is impregnated with a soln. of wax to which a dye or pigment has been added. Mixts. of beeswax and other waxes are preferred. A suitable prepn. consists of 8 lbs. of beeswax, 4 lbs. of ozokerite, 4 lbs. of Japan wax, 6 gals. of turpentine, and 2 oz. of sol. dye.

**Building material.** F. J. McALLISTER. U. S. 1,463,123, July 24. A mixt. suitable for the manuf. of building blocks is formed of sawdust, ground paper or other fibrous material 30-50, hydraulic cement 25-35, lime 5-10, alum 1-5 and siliceous material such as sand, cinders or diatomaceous earth 4-35 parts, with or without Na silicate.

**Plastic compositions.** J. SPERRI, R. B. G. GREIG and NURRODS, LTD. Brit. 191,265, Dec. 17, 1921. A compn. for constructional purposes consists of pulverized or granulated mineral material, comminuted ligneous material such as sawdust, wood pulp, or vegetable fiber, Portland cement, and Na silicate soln., with or without calcined magnesite and  $\text{MgCl}_2$  or stable coloring matter. The compn. may be hardened after molding by washing with  $\text{Na}_2\text{SiO}_3$  soln.

**Compositions for paving, roofing, etc.** L. CRESSON. Brit. 191,474, Oct. 12, 1921.

Mineral or fibrous materials are mixed with rubber latex or plastic coagulum; S, ZnO, dyes, and petroleum residues may be added. The mixt. is molded under pressure into blocks, slabs, etc., which may be partly vulcanized at this stage, a facing layer of latex, coagulum, or rubber mixt. is applied to the upper surface, and the whole is vulcanized together.

**Absorbent roofing felt material.** A. L. CLAPP. U. S. 1,463,611, July 31. An absorbent sheet is formed of fibers of "news" and chemical wood pulp mixed with an initially porous absorbent fireproof filler such as Kieselguhr.

**Composition for impregnating wood.** G. COESTER. U. S. 1,463,674, July 31. A mixt. for impregnating wood is prepd. by boiling together coal oil, bone oil and crude PhOH and condensing the vapors. This liquid when used as a primary coat leaves a heavy residuum in the condensing vat which is suitable for use as a finishing coat over the dried primary coat.

**Wood substitutes.** R. FREUDENBERG. Brit. 191,742, Jan. 11, 1923. A compn. consisting of sawdust to which may be added chips and peat, and an aq. soln. of albumin, water-glass and lime, is heated and submitted to a high pressure to make a substitute for wood.

## 21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

**The distribution of the forms of sulfur in Transvaal coal.** JAS. GRAY. *J. S. African Chem. Inst.* 3, No. 2, 12-6(1922).—The distribution of S in numerous grades of coal from different districts was studied by detg. the total S, S as sulfates, S as pyrites and S in org. compds. The total S was detd. by the method of Eschka, the org. S and S in pyrites by that of Powell and Parr (cf. *C. A.* 14, 112). The complete data are tabulated. No relation was found between total S and org. S. C. C. DAVIS

**Inorganic constituents of coal. IV. Melting point of coal ash.** F. S. SINNATT, A. B. OWLES AND N. SIMPKIN. *J. Soc. Chem. Ind.* 42, 206-72T(1923).—Previous work is reviewed and the authors' method of heating by an oxyacetylene flame, cylinders of pulverized ash,  $\frac{1}{32}$  in. diam. and  $\frac{3}{16}$  in. long mounted vertically on Pt foil, in a silica tube 1 in. external diam. and 6 in. long in a magnesia-brick furnace, is described. The temps. are taken with a Pt-PtRh thermocouple. Tables are given for the m. p. and analyses of ash from lump, slack and slurry of different coal seams, also of the ash from the different constituents of coal, viz.: Vitrain, clarain, durain, and fusain. The m. p. of the ash from different horizons in a seam, and from the different commercial grades of coal from the same seam varies within wide limits. The chemical analysis is of little value as a criterion of the m. p. of the ash. W. W. HODGE

**The constitution of coals. Possible commercial transformation. Hydrogenation of coal and of heavy oils.** A. STOUVENOT. *Mines, Carrières* 1, 57-9(1922); *Chimie et industrie* 9, 1153(1923).—A review. A. PAPINEAU-COUTURE

**The spontaneous combustion of coal in relation to its composition and structure.** MARIE C. STOPES AND R. V. WHITELER. *Fuel* 2, 123-32(1923).—New data and viewpoints are given in continuation of work already published (cf. *C. A.* 17, 2038). Tests were made to det. any differences in the behavior of durain (I), clarain (II) vitrain (III) and fusain (IV) on oxidation which might indicate differences in tendency to self-heating. To this end, the relative temps. of ignition by the previous method (*C. A.* 17, 2038) and the rates of absorption of O at different temps. by the "unsatd." coals by a new method were detd. I, II and III all had an ignition temp. (based on the points of intersection of the time-temp. curves), of 170-5°, but the wide differences in H<sub>2</sub>O content resulted in varying rates of rise in temp. below 80°. Judged by the rates of heating above 80°, II and III were equally likely to self-heat, and I was less likely. To det. the O-absorption rate, dried air or O was circulated through the sample in a horizontal tube maintained at a const. temp. Twenty g. of coal (10-60 mesh) were exhausted in the tube for 2 days first at room temp., then at 200°. When the coal was at the exptl. temp., gas was circulated through the closed system, initial readings of the pressure were taken and thereafter readings of the temp., pressure and barometer during 120 hrs. with a const. circulation of 1 l. of O per hr. through the coal. Graphs show the relation between time and vol. of O absorbed by I, II, III and IV at 15°, 50° and 100°. I, II and III absorbed O to a marked degree, but there was a decrease in absorptive power in the order III, II, I, which was particularly marked at low temps. (15°). At higher temps. (50°) the difference between III and II decreased and at 100° their absorptive power was nearly the same. I throughout the expts. had less absorptive power than

III or II, the O absorption by I being 10% less than by III at 15° and 30% less at 100°. IV stood apart from the rest in its high absorptive power at low temps., but at 100° its absorptive power was little more than I. Data on the exhaustion of oxidized coals at 200° showed (1) a rapid, continuous increase in the gas evolved (*i. e.*, the amt. of decompn. of the coal-O complex) as the temp. increased, (2) a variation in the degree of decompn. of the complex depending on previous treatment, which was greatest after the coal had been oxidized at 100° and exhausted at 200° (before this treatment oxidation at 50° and exhaustion at 200° released as CO<sub>2</sub> and CO 12% of the O absorbed at 50°, and subsequently 40%) and (3) a difference between I, II, III and IV in the ease of decompn. of the complex, the proportion of absorbed O released as CO<sub>2</sub> and CO being much less for II than for III or I (except after oxidation at 15°). Increase in temp. caused a rapid increase in the rate and in the total amt. of O absorbed. Even at room temp. the absorption was greater than can be accounted for by adsorption. Further expts. showed that when circulated over coal at 100° for several days (1) O contained no trace of H, (2) moist mixts. of CO and air did not change except from the action of O on the coal and (3) mixts. of H and air lost no H. In each expt. the usual formation of CO<sub>2</sub> and CO in a 2.4:1 ratio took place. Details of typical expts. made to establish these results are given. The chem. reaction following phys. absorption probably varies in degree and nature among I, II, III and IV. With IV, the O-complex either is formed less than in I, II and III, or when formed is more difficult to decomp. An historical survey of previous work on the "dull" and "bright" bands in ordinary coal is given.

C. C. DAVIS

**Fuel investigations.** F. JACOBSON. *Chem.-Ztg.* **47**, 527-8(1923).—A discussion opposing König's proposal (*C. A.* **17**, 2635) that the heat value of coal be calcd. from its water and ash content and its coke yield, by the formula  $H = (r/100)H_r - 600.(w/100)$  where  $H$  is the calorific value of raw coal,  $H_r$  that of pure coal after detn. of the pure coal content ( $r$ ) and the water content ( $w$ ) of the raw coal.

W. C. EBAUGH

**Powdered coal.** I. F. S. SINNATT AND L. SLATER. *Fuel* **2**, 142-6(1923).—Varying results obtained by different investigators on the oxidation of a coal are due to inadequate knowledge of the fineness, including errors due to different sieve standards and the different relative proportions of small to large particles in 2 samples passing through the same sieve. Examn. of many sieves (manufd. to have a screening area of 44%) showed a fair agreement with the specified mesh up to 150 mesh, but the 200-mesh sieves showed variations in the size of the mesh as great as 300%. Sieves finer than 200 mesh are not considered reliable. *Pulverizing tests on several grades of coal* in a cylindrical ball mill showed that there are marked differences in the rate at which different coals grind to a certain fineness. After a certain period of grinding (varying with each coal), the dust becomes coarser and less and less passes a 200-mesh sieve. This is due to formation of graphite-like flakes, indicating that simultaneous pulverization and agglomeration occur. Sieving tests do not det. the relative fineness of different coals even when the same % passes a given mesh, nor should the relative friability of coals be measured by the % passing a given mesh after grinding under const. conditions. The relative friabilities are modified by the time of grinding and for a short period 1 coal may have a friability relatively greater than another, whereas if the grinding is longer, the relative friabilities may be reversed.

C. C. DAVIS

**The wasteful use of coal.** ALLAN GREENWELL. *Fuel* **2**, 120-1(1923).—A plea for the proper utilization of different types of coal.

C. C. DAVIS

**Production of air-dried peat.** GEO. BEILBY. *Dept. Sci. Ind. Research (Brit.) Rept. Fuel Res. Board for 1922, 1923*, 146 pp.—Details are given of mechanical peat winning in Ireland, Canada, Sweden and Germany and the problems of large-scale production are discussed. The possible length of the season in Ireland is from Feb. 1 to Aug. 31. One ton of air-dried peat can be obtained from 80 sq. yd. of peat pulp spread to an av. depth of 4.5 in. About 2 spreadings can be made per yr. over the same area.

J. L. WILEY

**Tunisian lignites.** R. MARCILLE. *Chimie et industrie* **9**, 1239-43(1923).—Analyses are given showing H<sub>2</sub>O 5.8-34.6, results on dry basis: volatile 30.7-40.3, ash 13.2-34.4, fixed C 25.3-50.5, ratio of volatile to fixed C 0.72-1.59, S 5.23-9.4%. In 6 yrs. the Tunis Tramways Co. burned over 100,000 t. contg. 7-8% S without any abnormal deterioration of the surfaces in contact with the hot gases. The ash had the following compn.: SiO<sub>2</sub> 38.9, Fe<sub>2</sub>O<sub>3</sub> 28.4, Al<sub>2</sub>O<sub>3</sub> 14.0, CaO 9.4, MgO 2.7, SO<sub>3</sub> 5.2, P<sub>2</sub>O<sub>5</sub> 0.22%, m. p. about 960°. Analysis of one sample was: H<sub>2</sub>O 5.80, ash 21.61, C 48.55, H 3.53, volatile S 7.30, N 0.86, O 12.35%, calorific value (by Mahler's bomb) moist 5,020, dry 5,330, on ash-free basis 6,920, calcd. on dry basis 6,110 cal. soly. in benzene 1.4, in PhNH<sub>3</sub> 6.4, in pyridine (35 hrs. in Soxhlet) 20.0, in boiling 10% KOH (6 hrs.) 5.5%.

Lignites contg. 18–23% ash and 5–7% H<sub>2</sub>O on distg. to 450° gave H<sub>2</sub>O 11–14, tar 6–8.5, gas 6–10, coke 70–5%. Further heating to 700–800° gave only 1.5% tar and 8.6% gas. The gases collected at the beginning and at the end of distn. had the following resp. comps.: CO<sub>2</sub> 52.4, 35.8; C<sub>2</sub>H<sub>4</sub> 5.6, 5.5; O 0.6, 1.7; CO 5.3, 1.9; CH<sub>4</sub> 21.1, 26.4; H 2.6, 12.7; N 12.5, 16.0%. The compn. of the dry and filtered low-temp.-distn. tar was: bitumen 0.9, liquid hydrocarbons 72.8, solid hydrocarbons 0.5, hydroxy acids 0.52, insol. fatty acids 0.42, sol. fatty acids 1.12, phenols 21.64, loss 2.1%. Distn. in a Luynes-Bordas still after drying gave: light oil (to 200°) 0.8, medium oil (to 290°) 35.0, heavy paraffin oil (to 390°) 38.6, pitch about 16%. The fractions would require considerable purification. The tar could readily be treated to sep. light hydrocarbons and paraffin, the residue being used as fuel oil, with approx. yields of 7, 1 and 90%, resp.

A. PAPINEAU-COUTURE

**The scientific study of liquid fuels.** DANIEL BERTHELOT. *Chimie et industrie Special No.*, 71–9(May, 1923).—An address on national liquid fuels. A. P.-C.

**Some laboratory tests with the (French) national fuel.** GODCHOT AND GAY. *Oil Eng. Finance* 2, 484–5(1922).—Cresol, cyclohexanol and butyl alc. have been found to be good common solvents for motor fuel mixts. Acetone is moderately good. Also in *Chimie et industrie Special No.*, 731–2(May, 1923). D. F. B.

**A study of mixtures of petrol and alcohol.** H. GUINOT. *Oil Eng. Finance* 2, 488(1922).—K<sub>2</sub>CO<sub>3</sub> becomes effective as a dehydrating agent when petrol is added to alc. The spirit so obtained is stabilized by adding 1 to 2% of a powerful solvent such as butyl alc. and is further improved by adding small quantities of other liquids like benzene, ether or alc. Isopropyl alc. is a good denaturant. This compd. yields with water a const. boiling mixt. of b. p. 80°. It is impossible to remove this substance on a practical scale and it is a powerful solvent for mixts. of alc. and petrol. Also in *Chimie et industrie Special No.*, 722–8(May, 1923). D. F. B.

**Scientific organization of the congress held at Beziers for a national motor spirit.** GODCHOT, PASQUER, ROBERT AND GAY. *Oil Eng. Finance* 2, 438(1922).—Tests show that a fuel composed of 10–20% of 95% alc. can be used without modifying the engine in any way. Further addn. of alc. diminishes the power unless the engine is modified. A 250-km. test over hilly roads gave 20 km. per l. with a 10% alc. (95%) and 90% gasoline mixt. with a small quantity of cyclohexanol and phenol. Also in *Chimie et industrie Special No.*, 714–7(May, 1923). D. F. B.

**The burning of tar oils in Diesel engines.** M. JUNIEN. *Oil Eng. Finance* 2, 487(1922).—Analyses of different tar oils are compared with those of mineral and vegetable oils and the qualities to be specified for tar oils and the best way of obtaining these qualities are discussed. Use of tar oils in Diesel engines is described and emphasis laid on the necessity of greater production of this kind of fuel in France to minimize the necessity of importing fuel. Also *Chimie et industrie, Special No.*, 609–24(May, 1923). D. F. B.

**Evolution of a chemical industry.** CHARLES CARPENTER. *J. Soc. Chem. Ind.* 42, 289–94T(1923).—An historical review of the development and present problems of the coal-gas industry. T. S. CARSWELL

**Two analytical determinations for illuminating gas. The comburent power and the nitrogen content.** M. NICLOUX. *Bull. soc. chim.* 33, 823–35(1923).—The *comburent power* is defined as the no. of vols. of air necessary for the perfect combustion of 1 vol. of the gas. To det. the air required for perfect combustion add an excess of air and explode the mixt. Remove CO<sub>2</sub> by caustic alkali and the residual O<sub>2</sub> by absorption in alk. hyposulfite. The N<sub>2</sub> can be detd. by measuring the total vol. and allowing for the N in the air added. Instead of adding air it is better to add O<sub>2</sub>. Analyses of gas at Strassburg and at Paris show that the quality of the gas has deteriorated in both places since 1914 but the deterioration is more marked in the Strassburg gas. D. F. B.

**A comburimeter and a controller for gas, according to the Grebel-Velter system.** A. GREBEL. *Compt. rend.* 174, 1285–8(1922).—An app. for measuring the comburent power (cf. preceding abstract) is described. It consists essentially of a combustion chamber in which the flame is free to burn with a regulated vol. of air, and a control chamber where the burned gases are exalnd. to det. the degree of combustion. To det. the state of oxidation molten Pb is used, neutrality of combustion being characterized by the disappearance of iridescent streaks, due to PbO, which form with excess air. C. C. DAVIS

**Great Britain points the way in low-temperature carbonization.** C. H. S. TUPHOLME. *Chem. Met. Eng.* 29, 142–5(1923).—Low-temp. carbonization is attractive in England because of smoke damages and the need of motor and fuel oils and of NH<sub>3</sub>.

for agricultural development. Of the 188,000,000 tons of coal used per year, 140,000,000 tons might be available for low-temp. carbonization. This would yield 400,000,000 gal. of motor spirit, 59,000,000 bbl. of coalite oil and 1,000,000 tons of  $(\text{NH}_4)_2\text{SO}_4$ . The semicoke with 9-10% volatile is a superior smokeless fuel. The gas, of 700° to 750° R. t. u./ft.<sup>3</sup>, might be used instead of oil for enriching town gas. Temps. of 600° to 750° are used. The lower temp. is desirable for higher oil yields, the higher, for firmer semi-coke. For semi-coke of the best quality a certain quantity of resins which decompose at 550° to 750° should be present. This may be assured by mixing coals. The slow development of low-temp. carbonization is due to (1) slow evolution of suitable retorting app., (2) inadequate knowledge of coal compn. and thermal decompn., (3) non-existence of markets for the rather special products. The first commercial application will probably be to the coal used for domestic purposes.

**Gas-producer heat balances.** W. B. CHAPMAN. *Glass Worker* 42, No. 39, 11, 18, 20 (1923); *Glass Ind.* 4, 123-6 (1923).—A pyrometer recording the sensible heat of the producer gas is recommended as an aid to correct producer operation. A heat balance is offered as a tentative standard compiled from tests of 12 different installations of mech. producers of 4 different makers.

**Producer gas and gas-producer practice.** III. R. V. WHEELER. *Fuel* 2, 156-60 (1923); cf. *C. A.* 17, 2948.—An illustrated description, including producer construction, the grate, solid-bottom producers, bar-bottom producers,  $\text{H}_2\text{O}$ -bottom producers, the body of the producer, the charging hopper, the method of supplying the blast and the use of the superheated blast.

**Fuel Research Board. II. Steaming in vertical retorts.** ANON. *Engineering* 115, 734-6, 761, 811-2 (1923); cf. *C. A.* 14, 2251, 2252; 15, 2711.—The main purpose of the installation of 4 Glover-West vertical retorts at the Fuel Research Station and of the work done on them was to provide accurate data from which the economic value of steaming could be detd. The problems sought to be solved were the effect on the yields and qualities of gas, tar, coke and  $\text{NH}_3$  produced with different types of coal by a definite amt. of steam at a definite carbonizing temp., and the amt. of extra heat required for an increased yield of products. Two tests were made as nearly as possible in parallel with tests made at Uddingston by the Gas Investigation Comm. (*C. A.* 14, 2409). The setting was fired with scrubbed water gas supplied from outside under const. pressure. An av. temp. of about 1250° was maintained in the combustion chambers. The general design and the operation of the plant are described and the details of testing, analysis, and of calcg. the thermal balance are discussed. Three types of coal were used: Durham, South Yorkshire and Lanarkshire, and the general results obtained for each type are compared. In general, more gas per ton of coal was obtained in all tests with steam than from those on the same coal without it. The calorific value of the additional gas was increasingly lower as the % of steam, calcd. on the wt. of coal, increased above 5%. Up to this point the calorific value was greater than without steaming and the steam was entirely decomposed, whereas the % of decompn. fell rapidly with further increase till with 30% of steam only 52.3% was decomposed. In every test the vol. of gas made with increased steaming increased more than the calorific value fell off, so that there was always an increased yield of potential heat in the total vol. of gas made per ton of coal. In every test the yield of coke as well as the calorific value was less with steam than without and the % of breeze was greater. The yields of tar and of  $(\text{NH}_4)_2\text{SO}_4$  also were greater with steaming. As to the thermal cost of the process, considering only the heat supplied in the fuel gas and steam and in addition to what was used to maintain the carbonizing temp., with 5% of steam the make of gas per ton of coal was obtained with fewer therms in fuel gas and steam than were required without steam while the heat in the gases was several therms greater. At higher % of steam the heat required exceeded that used in carbonizing without steam, but up to a limit varying with the coal, the heat that had to be added was less than was gained in the make of gas. From the point of view of the heat value of the gas to be made for a given supply of fuel gas, the max. % of steam that could be used with no more fuel gas than is required in carbonizing without steam, were 15 for Durham coal, 12.5 for Yorkshire and 10 for the Scottish. Further heat value in the make of gas requires the supply of more fuel gas. In calcg. the thermal cost of the process consideration is also given to the consumption of coke in the retorts and to its change in calorific value as the % of steam changes, and to the heat value of the tar. A comparison of the results with the thermal cost of enriched water gas shows that the retort gas obtained by steaming is produced at about half the thermal expense of the enriched water gas, and even less in the very low % of steam, when the increased yield per ton is obtained with no more heat than is required for the lower yield without steam, or even with less. The actual

limit of economical steaming cannot be stated in general terms; but the results demonstrate that by moderate steaming at moderate temps. the heat value of the gas from a setting of vertical retorts can be greatly increased and the cost per therm reduced.

J. L. WILKY

**Gasification of coke in steam, with special reference to nitrogen and sulfur.** S. PEXTON AND J. W. COBB. *Gas J.* 163, 160-73 (1923); *Gas World* 78, 619-30; cf. Monkhouse and Cobb, *C. A.* 16, 333, 2767.—Detn. was made of the action of steam on 3 cokes made from Blackwell coal: *A* 800° lab. coke, *B* 1100° lab. coke, and *C* by-product oven coke. The amts. of steam used and the temps. of gasification were varied in order to permit of the study of the formation of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  under various conditions. When coke *A* was gasified, the C-N ratio in the residue increased in the early stages and then remained substantially const. at a higher value than in the original coke. The gasification of the N relative to the C seemed independent of the temp. of gasification and the amt. of steam used. When gasified at 900° in an amt. of steam similar to that used in a water-gas generator, little  $\text{NH}_3$  survived dissociation. Trebling the amt. of steam used did not alter the relative % rates of gasification of the C and N, but so reduced the amt. of  $\text{NH}_3$  dissociated that practically complete recovery of the N as  $\text{NH}_3$  resulted. Coke *A* gasified at 950° with twice the velocity with which it gasified at 900°. The excess of steam was large and 60-70% of the gasified N was recovered as  $\text{NH}_3$ . At 1000° very little N was recovered as  $\text{NH}_3$  even in presence of a large excess of steam. At 800° the gasification was much slower than at 900° but the mode of liberation of the N and the S was similar for the 2 cases. Cokes *B* and *C* when gasified in liberal amts. of steam at 900° yielded almost identical results. N was evolved at the same % rate as the C and the C-N ratio in the residue remained const. throughout gasification. The behavior of the S depended upon the rate of gasification of the C, which in turn depended largely upon the temp. of gasification and the treatment the coke had received during prepn., upon the concn. of steam in the gases leaving the coke, and upon the proportional amts. of different S constituents in the coke. In presence of a large excess of steam, the sulfide constituents in the coke decomposed rapidly in the early stages of gasification. This was most marked in cases where the velocity of gasification of the C was low. When the bulk of the sulfides had been decomposed, the remaining S existing in close association with the C was gasified simultaneously with it and a const. C-S ratio in the coke residue was established. The max. extent to which cokes could be desulfurized with little gasification of the C seemed to be governed primarily by the proportion of sulfide S in the coke. The S curve for the gasification at 1000° differed from that at 900° because the high rate of gasification of the C at that temp. masked the early independent decompn. of the sulfide S. In all expts. substantial equivalence existed between the S gasified and that recovered in the  $\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_2$  washers. The velocity of gasification at the same temp. of different cokes from the same coal depended on their mode of prepn. The av. velocities of gasification of cokes *A*, *B* and *C* were approx. 1.75:1:1. The velocity of gasification of the same coke increased with temp. The velocities for coke *A* at 800°, 900°, 950° and 1000° were as 1:6:14:22. The av. temp. coeff. for the velocity of gasification between 800° and 1000° was 1.16. The actual velocity of gasification of coke *A* at 900° was 30% of the av. amt. of coke present per hr. The mode of combustion in steam normally appears to be an increase in porosity as gasification proceeds, with very little alteration in size until mech. collapse of the weakening structure begins.

J. L. WILKY

**Report on the complete gasification of coal.** R. G. PORTER. *Am. Gas Assoc. 4th Ann. Convention, Tech. Sec. 4*, 103-31 (1922).—The economic possibilities of complete gasification in the U. S. are discussed and the Tully, J. U. McDonald, and Doherty processes are described. A bibliography is given.

J. L. WILKY

**Complete gasification of coal.** J. S. G. THOMAS. *Nature* 111, 778-9 (1923).—Discussion without conclusions on the Tully plant and the possibility of its combination with a synthetic  $\text{CH}_4$  plant.

J. J. MORGAN

**Ninth report of the Research Sub-committee of the Gas Investigation Committee of the Institute of Gas Engineers.** Study of atmospheric burners, aeration and air injection. J. W. WOOD. *Gas J.* 163, 104-18 (1923); *Gas World* 78, 589-98; cf. *C. A.* 16, 2769.—If the pressure and with it the gas rate are increased, in working with the same burner and gas nipple with any one grade of gas, there is in the early stages a rapid increase in the degree of aeration. Above 2 in. water pressure the further increase in the degree of aeration with increase in pressure and gas rate is much smaller, and the air-gas ratio approaches a steady value. In most cases, if the same injection tube and gas nipple are used, but the sp. gr. of the gas is increased, for the same gas pressure, the vol. of air drawn in is unchanged—i. e., the air-gas ratio is inversely as the gas

rate. At equal gas rates with the same burner and nipple, the degree of aeration increases with the sp. gr. of the injecting gas. Increasing the outlet resistance of a burner by reducing the total outlet area diminishes the degree of aeration. A limit is placed on the extent to which burner resistance can be lowered by increase of outlet area, owing to the fact that the velocity of efflux of the mixt. must be suitably related to its rate of flame propagation. Shortening the mixing tubes materially increases the degree of aeration. If the sp. gr. of the gas and its pressure are fixed for a particular burner, but the gas rate is adjusted by varying the size of the nipple, the abs. amt. of air drawn in will increase with increasing size of nipple. The air-gas ratio, however, will fall. With const. sp. gr., pressure, and B. t. u. consumption, but with reduced calorific value of gas, the larger nipple will produce a lower air-gas vol. ratio, but the degree of aeration expressed as a % of the air requirement for complete combustion will in general be increased. Back-firing may prevent the employment of the full amt. of air which an appliance is capable of injecting. Special adjustment may be necessary to utilize certain gas mixts., such as blue water gas, with a high proportion of their theoretical air requirement as primary air. It has not been found possible to deduce the degree of aeration of a burner, even approx., by equating the momentum of the issuing air-gas mixt. to the momentum of the injecting gas-jet issuing from an orifice under prescribed conditions. This applies with greater force to the kinetic energies of injecting gas-jet and air-gas mixt. The work of the Am. Bur. Standards as well as that of other investigators is reviewed.

J. L. WILEY

**Report of the Builders' Section.** J. H. TAUSSIG, *et al.* *Am. Gas Assoc. 4th Ann. Convention, Tech. Sec. 4*, 135-210(1922).—Reports on construction and improvements in design are given of the following companies and app.: the Roberts Oven, charging and discharging machines of the Bartlett Hayward Co., the By-Product Gas Ovens of the Gas Machinery Co., Glover-West Continuous Vertical Retorts, Woodall Duckham Continuous Retorts of the Isbell-Porter Co., the Koppers Co. Combination Oven, the carbonizing app. of the Parker-Russell Mining and Mfg. Co., Dessau Vertical Coke Ovens, the Smet-Solvay By-Product Coke and Gas Ovens, the U. G. I. Vertical Retorts.

J. L. WILEY

**Internally heated retorts.** C. V. MCINTYRE. *Am. Gas Assoc. 4th Ann. Convention, Tech. Sec. 4*, 76-93(1922).—The following processes are briefly described: Those heated by producer gas; the MacLaurin, Sutcliffe-Evans, Neilson, Bussey, Mond, Ziegler, and Messel processes; the Tri-gas Generator process heated by water gas; the Pritchard process heated by coal gas; the Lamplough process heated by superheated steam; the Frank and the Pintsch processes heated by the products of combustion. The possibilities of these processes in the U. S. are discussed.

J. L. WILEY

**Use of mixture of bituminous coal and coke as generator fuel in a water-gas set.** C. W. BRADLEY, *et al.* *Am. Gas Assoc. Monthly 5*, 49-59(1923).—With different sizes of water-gas sets, when coal and coke mixts. are used, the rate of production tends to a max. and the fuel consumption per 1000 cu. ft. of gas is lowest when a mixt. contg. 70-80% of coal is used.

J. L. WILEY

**Deposits in gas pipes and meters.** R. L. BROWN. *Am. Gas Assoc. 4th Ann. Convention, Tech. Sec. 4*, 280-311(1922); cf. *C. A.* 17, 201, 869.

J. L. WILEY

**Proper scrubbing and condensing facilities in a coal-gas plant and their effect upon tar and ammonia recovery.** J. R. WOHRLEY. *Am. Gas Assoc. 4th Ann. Convention, Tech. Sec. 4*, 349-87(1922); cf. *C. A.* 17, 624.

J. L. WILEY

**Some observations on the use of the Doherty washer cooler as a water-gas condenser.** F. W. STEERE. *Am. Gas Assoc. 4th Ann. Convention, Tech. Sec. 4*, 335-48(1922); cf. *C. A.* 16, 4328.

J. L. WILEY

**Outside producers at Racine.** H. R. BROKER. *Am. Gas Assoc. 4th Ann. Convention, Tech. Sec. 4*, 10-21(1922); cf. *C. A.* 16, 1656.

J. L. WILEY

**Carbonization of coal with blue gas and producer gas.** W. R. MORRIS. *Am. Gas Assoc. 4th Ann. Convention, Tech. Sec. 4*, 21-52(1922); cf. *C. A.* 17, 1317.

J. L. WILEY

**Ammonia yields from vertical retorts.** GEO. BRAIDWOOD. *Gas J.* 163, 180-9(1923); *Gas World* 78, 637-46.—In order to obtain max. yields of  $(\text{NH}_4)_2\text{SO}_4$ , fairly heavy steaming coupled with moderate retort temps. should be practiced. With 40% steaming and the temps. in the combustion chamber graduated from 731° at the top to 1127° at the bottom of the settings, a yield of 48.96 lb. of  $(\text{NH}_4)_2\text{SO}_4$  (24.75%  $\text{NH}_3$ ) per ton of wet coal was obtained. With 20% of steam and av. temps. of 1108°, the yield fell to 39.52 lb. The presence of large amts. of H is not of importance either in the formation or preservation of  $\text{NH}_3$ . Blue water gas was introduced but with no beneficial effect in the formation of  $\text{NH}_3$ ; the yield of sulfate fell as the % of steam was

reduced. The size of the material carbonized appears to have no effect on the yield of  $\text{NH}_3$ . Heavy steaming does not necessarily mean low-quality gas, as in one test, with low top temps. in the retort, the gas quality was maintained at 464 B. t. u. per cu. ft.

J. L. WILEY

**Recovery of benzene in small gas works.** A. BARIL. *Oil Eng. Finance* 2, 485 (1922).—Coal gas yields about 30 g. of benzene per cu. m. Benzene recovery is not possible for small plants producing 2000–4000 cu. m. per day. Processes in use consist in absorbing the benzene in either heavy tar oil which absorbs 3% of its wt., or in tar, or in a mixt. of cresols and phenols which absorbs 5–10% of its wt., followed by steam distn. Other patents are known such as absorption in charcoal or in China clay impregnated with oil and heated. Also in *Chimie et Industrie Special* No., 559–63 (May, 1923).

D. F. B.

**Recovery of benzene by Bayer's process.** P. GREGORY. *Oil Eng. Finance* 2, 485 (1922).—This process is employed at Leverkusen's gas works, which produces 2000 cu. m. of gas per day, yielding 33 g. of benzene per cu. m. Charcoal treated with  $\text{ZnCl}_2$  and heated is the absorbent. Two filters are placed in a parallel position, one for the absorbent stage and one for the recovery. The absorption capacity of the charcoal is about 40% of its wt. The filters have a cubic capacity of 780 l. and contain about 600 kg. of charcoal each. The depth of the charcoal is about 1 m. To recover the benzene superheated steam is injected into the filter and 90% is recovered in about 20 min. The remaining 10% is harder to recover, more steam and a temp. of 120° being required. The process is claimed to be very economical. Also in *Chimie et Industrie Special* No., 564–9 (May, 1923).

D. F. B.

**Determination of naphthalene.** T. WERNER. *Gas u. Wasserfach* 66, 257 (1923).—Mezger's method (C. A. 15, 3201) modified by Offe (C. A. 17, 1882) can be further simplified by directly titrating the pptd. picrate with KOH instead of titrating the excess of unused picric acid.

J. L. WILEY

**Provan Chemical Works of the Glasgow Corporation.** ANON. *Engineering* 115, 761–4, 792–4 (1923).—The plant as described is most completely equipped for the recovery of by-products and derivatives and their purification in connection with gas manu.

J. L. WILEY

**Institution of Gas Engineers. Sixtieth annual meeting. President's address.** J. D. SMITH. *Gas J.* 163, 95–100 (1923); *Gas World* 78, 579–84.—Conditions in Belfast are described.

J. L. WILEY

**Report of Life of Gas-Meters Joint Committee.** B. R. PARKINSON. *Gas J.* 163, 190–1 (1923); *Gas World* 78, 646–8; cf. C. A. 16, 2771.—General review.

J. L. WILEY

**Gas cleaning.** ROY U. WOOD. *Glass Ind.* 4, 106–7 (1923).—The Cottrell elec. pptn. process applied to producer gas is described.

J. B. PATCH

**Latest developments in gas purification.** E. H. BIRD. *Chem. Met. Eng.* 29, 16–8 (1923).—Additional data are given on construction of absorber and actifier units, tower packing, disposal of actifier air and plant operation in connection with gas purification by the *Koppers liquid process*. Efficiencies of removal of  $\text{H}_2\text{S}$  at some principal plants are: 91% at the Seaboard By-Products Co. with a consumption of 0.062 lb. of soda ash per 1000 cu. ft.; 89.1% at the Battle Creek Gas Co. with a consumption of 0.0188 lb. of soda ash; 75% at Rochester; 93% at Indiana Coke & Gas Co.

J. L. WILEY

**Methods of transferring heat to the coal mass in low-temperature carbonization with externally heated retorts.** H. A. CURTIS. *Am. Gas Assoc. 4th Ann. Convention, Tech. Sec.* 4, 94–100 (1922).—A brief discussion is given of coking coal in thin sheets at low temp. as in the Coalite, Tozier or Wallace processes, which have the disadvantage of low capacity per retort, and coking with agitation of the charge as a means of increasing retort capacity as in the Carbocoal process.

J. L. WILEY

**Lignite gas and its use in the ceramic industry.** ALFRED FABER. *Z. angew. Chem.* 36, 336–7 (1923).—A review and description.

C. C. DAVIS

**The treatment of mineral fuels for the production of liquid fuels.** CH. BERTHELOT. *Compt. rend. trav. soc. ing. civils France* 75, 345–59 (1922); *Chimie et Industrie* 9, 1141–2 (1923).—A review.

A. PAPINBAU-COUTURE

**Low-temperature tar and its evaluation.** J. D. DAVIS. *Am. Gas Assoc. 4th Ann. Convention, Tech. Sec.* 4, 65–76 (1922).—Economic considerations in the production of low-temp. tar are reviewed. In the U. S. it may pay to develop a low-temp. carbonization industry primarily for the production of a domestic fuel with motor spirit as a liquid by-product. Present established carbonization industries would not be greatly affected.

J. L. WILEY



**The determination of the burning characteristics of cokes.** F. HÄUSSER. *Stahl u. Eisen* 43, 903-7(1923).—The specifications of cokes at the present time pay no attention to the characteristic burning qualities but merely to the chemical analysis. The ratio of CO to CO<sub>2</sub> produced is the basis for the calcn. for the detn. of burning qualities. The temp. also enters the calcn. when long columns of the coke are used; the gases thus leave the coke at lower temps. with the deeper columns. From the detns. of Berger (*Kruppsche Monatshefte* 4, 57-64(1923)) with small tests, the burning depends entirely upon the porosity and not on the coking temp. During combustion CO<sub>2</sub> is first formed and then is more or less reduced to CO on passing through the glowing coke; and the faster these reactions take place, the more combustible is the coke. The greater the amt. of CO<sub>2</sub> formed, the greater the temp., and the more conversion to CO. The total conversion is designated by  $(CO_2 + CO)/O_2 = \Sigma C/O_{max}$ , for the complete conversion of C. Corrections are made in some cases for the diff. temps.

W. A. MUELLER

**New view-point on the formation and nature of coke.** F. BÖSSNER. *Z. Ver. Gas u. Wasserfach.* 63, 22-6(1923).—Theories of coke formation and reasons for easy or difficult combustibility of coke are reviewed with the conclusion that combustibility depends upon porosity rather than upon compn. Porosity decreases with increasing temp. of carbonization. At low temps. the evolution of gas in the plastic mass yields a highly porous semi-coke with almost the properties of activated carbon. Semi-coke is especially suitable for use as powd. fuel. At higher temps. the decompn. of gases on the walls of the pores deposits carbon, decreasing porosity and combustibility. Coke for easy combustibility should be made at temps. not higher than 750° to 825° or 850°. The nature of the coal plays an important part. Mixing coals, as practiced in America, and grinding the mixt. improve the coke. Moisture from quenching should be kept low. A low ash content can be obtained by using washed coal.

J. J. MORGAN

**The dry distillation of lignin and cellulose.** FRANZ FISCHER AND HANS SCHRADER. *Gas. Abh. Kenntnis Kohle* 5, 106-10; *Chem. Zentr.* 1922, III, 1184.—The amt. of H<sub>2</sub>O obtained by the distn. of cellulose is more than twice that from lignin (33:13) and the crude tar nearly twice as great (23:12). Since the amt. of gas is approx. the same (37:34), cellulose yields less than 0.5 the amt. of semi-coke that lignin does (25:57). For cellulose, the neutral constituents of its crude tar (31% by wt.) are greater than the acid constituents (8% phenols, 9% constituents reacting with Na<sub>2</sub>CO<sub>3</sub>), whereas the opposite is true of lignin (neutral constituents 13%, phenols 34%, strongly acid compds. 16%). The high losses are due to the soly. of part of the crude tar in H<sub>2</sub>O. The yield of tar from cellulose is very high (21-4%).

C. C. DAVIS

**From coke oven to by-product market, Rosedale refinery.** G. A. RICHARDSON. *Und. Age* 24, 201-7(1923); cf. *C. A.* 17, 2931.—The plant and the processes are described.

H. H.

**The application of coke-oven gas to the synthesis of ammonia.** G. CLAUDE. *Compt. rend.* 176, 394-6(1923); cf. *C. A.* 15, 2340.—Coke-oven gas is taken from the debenzolizing app., compressed up to 25 atms., scrubbed with a heavy oil to debenzolize it further. This increases the yield of light oil from 10 to 15%. The gas is then scrubbed with lime water to remove CO<sub>2</sub>, and then passed to the liquefying app. where the H<sub>2</sub>O, ethylene, etc., are removed and recovered for use, the latter possibly being used to manuf. EtOH. H is obtained as a final product from this app. and is sent to a gasometer; the gas residue being now rich in CH<sub>4</sub> is returned to the ovens. The H is drawn with a suitable amt. of air (the O of the air being removed through combustion with some of the H) into a compressor and then passes through the usual purifiers and catalyzer chambers to form NH<sub>3</sub>. The elec. energy consumed is about 2.5 kw. hr. per kg. of NH<sub>3</sub>, 850 cu. m. of gas having 49% H, giving 150 kg. of NH<sub>3</sub> of which 140 kg. are liquid. The power required includes heating, removal of CO<sub>2</sub> and final debenzolization, 1.5 kw. hr. being required for the synthesis and 1 kw. hr. for the remaining operations. Two-thirds of the initial calorific value is left in the gas returned to the ovens. Advantages claimed are low first cost, 10 to 15% increased yields of light oils, reduced vol. of debenzolizing and stripping app., a yield of ethylene sufficient to manuf. 150 to 200 kg. EtOH per metric ton of NH<sub>3</sub>.

P. D. V. MANNING

Fifty-ninth annual report of the Alkali Inspector (BAILEY) 18. Coke and its behavior in the foundry (KOPPERS) 9. Adsorption and adhesion pressure (TRAUBE, NISHIZAWA) 2. Coke quality and blast-furnace operations (SPERR, JACOBSEN) 9. Lignite primary tar (FROMM, ECKARD) 10. Gravity separation of coal (U. S. pat. 1,462,881) 13.

**Liquid fuel.** J. A. LEADBEATER. Brit. 191,201, Oct. 20, 1921. A fuel to be sprayed on to the bed of a furnace is prep'd. by grinding into a very fine or colloidal state about 5–10 parts of wet peat, 1 part of tallow, soap, or other fatty substance, and 30 parts of coal or other carbonaceous solid, mixing in about 59–64 parts of crude oil such as petroleum or tar oil, and then passing the whole through the grinding machine or through Plauson's or other colloid mill.

**Process of burning pulverized fuel in which portland cement is obtained as by-product.** TSUNRICH FUJIYAMA. Japan. 43,420, Sept. 8, 1922. CaO and small amts. of SiO<sub>2</sub> or other similar substances are mixed with pulverized fuel in such proportion that portland cement is formed in the ashes of the fuel. The pulverized mixt. is burned with air blast to heat boilers or other app. and to produce cement clinker at the same time.

**Controlling combustion in boiler furnaces.** F. H. BROWN. U. S. 1,463,141-2-3, July 24. Fuel feed is automatically regulated by variations in furnace pressure or out-flow of furnace gases.

**Oil gas.** E. ROBINSON and M. ROBINSON. Brit. 191,411, Oct. 11, 1921. An auxiliary steam boiler supplies steam to a heater contg. heating coils, through which hydrocarbon and H<sub>2</sub>O circulate; the hydrocarbon and H<sub>2</sub>O then pass to a retort which is heated by superheated steam to a temp. sufficient to vaporize the liquids. A suitable construction is specified.

**Heating checkerwork.** R. VUILLEUMIER. U. S. 1,460,046, June 26. The checkerwork of a gas-making app. or similar device is uniformly heated by leading in gases upwardly through the checkerwork, withdrawing a portion of the gases from the upper side of the checkerwork after the latter has been partially heated, and leading the gases thus withdrawn into those at the lower side of the checkerwork to reduce the temp. of the gases entering the checkerwork.

**Distillation apparatus for coal.** CHINGEN KANEKO. Japan. 41,618, Jan. 31, 1922. A zigzag tube made of refractory brick is constructed in an oven of refractory brick. Coal is gradually charged into the tube from the top. Coalite of high quality, coal gas, tar, etc., are produced.

**Coking coal.** S. R. ILLINGWORTH. U. S. 1,462,576, July 24. Coal is heated out of contact with air to destroy the non-coking substances in the coal but to leave 5% of the resinic substances in the product in order to prevent expansion of the coke during the coking process and the preheated coal thus prep'd. is then coked at a temp. of 450–500° or slightly higher. Cf. C. A. 17, 336, 1884.

## 22—PETROLEUM, LUBRICANTS, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

**French laboratories for pure research and applied science. The Petroleum Institute, Strasbourg.** ANON. *Recherches et inventions* 4, 567-76(1923).—A detailed illustrated description. A. PAPINEAU-COUTURE

**The standardization of the tests for petroleum and its products.** A. E. DUNSTAN. *Chimie et industrie Special No.*, 212-25(May, 1923); cf. C. A. 17, 204.—An account of the work done to date by the Committee on Standardization of the Institution of Petroleum Technologists. A. PAPINEAU-COUTURE

**The use of super-centrifuges in the petroleum industry.** R. BERLINE. *Chimie et industrie Special No.*, 170-4(May, 1923).—Brief description of the use of Sharples super-centrifuges in America for dehydration, purification, and separ. of paraffin from petroleum. A. PAPINEAU-COUTURE

**Madagascar petroleum.** A. MERLE and H. GAULT. *Chimie et industrie Special No.*, 175-7(May, 1923).—See C. A. 16, 4332; 17, 2046. A. PAPINEAU-COUTURE

**Control of evaporation.** C. P. BUCK. *Petroleum Age* 12, No. 2, 26-30, 72(1923); cf. C. A. 17, 2779.—Evapn. expts. were carried out in a small welded tank under conditions resembling field conditions for storage tanks. Vapor pressures as high as 5 lbs. in the tank were recorded. These pressures depend on the gravity and freshness of the oil and increase with the temp. of the vapor, which is greatly influenced by the direct rays of the sun. A drop in temp. causes condensation of vapors resulting in formation of vacuum in the tank. Gas tight tanks must therefore be strong enough to withstand these variations in pressure. Wild gas has a larger v. p. and must not be admitted into the tank. Safety valves for excess pressure and vacuum must be pro-

vided. Four lease tanks were connected by a 2-ft. pipe 750 ft. long to a lease boiler and sufficient vapor was produced by evapn. alone to fire the boiler steadily throughout the daylight hours. D. F. BROWN

**Developments in the field of mineral oil analysis and the mineral oil industry during 1918-9.** I. SINGER. *Petroleum Z.* 18, 10, 52, 83, 119, 173, 206, 247, 287, 325, 363, 410, 447, 493, 589, 638, 704, 743, 806, 903, 936, 994, 1073, 1197, 1247, 1279, 1302, 1416, 1448, 1485(1922). D. F. BROWN

**The Roumanian petroleum industry.** L. JOHNSTON. *Petroleum Times* 10, 5-8 (1923).—The present situation of the industry in Roumania is outlined with reference to production, transportation, refining, laws, etc. D. F. BROWN

**Galician petroleum.** GEORGES NICLOUX. *Chimie et industrie Special No.*, 97-114 (May, 1923).—A description of the Galician oil field and of the methods used in working it. A. PAPINEAU-COUTURE

**The Argentine petroleum oil fields.** CAMPBELL M. HUNTER. *Chimie et industrie Special No.*, 118-21 (May, 1923).—Brief description. A. PAPINEAU-COUTURE

**The preparation of petroleum from vegetable and animal oils.** A. MAILHE. *Chimie et industrie Special No.*, 80-8 (May, 1923).—A review of M.'s work on this subject. See C. A. 15, 3739, 3741; 16, 639, 2306, 2787, 3304, 3467, 3870, 4077; 17, 197, 263, 1195, 1885. A. PAPINEAU-COUTURE

**Terminology and physical and chemical characteristics of petroleum products.** F. BORDAS. *Chimie et industrie Special No.*, 89-94 (May, 1923).—A discussion of the necessity of precise and clear definitions, with a list of the com. products derived from Pechelbronn petroleum, of com. benzene and tar products, and of com. products from Autun bituminous shale products, and of their chief properties. A. P.-C.

**The hydrogenation of mineral oils and similar products by the Bergius process.** H. I. WATERMAN AND J. N. J. PERQUIN. *Chimie et industrie Special No.*, 200-7 (May, 1923).—The functions of cracking and of hydrogenation in the Bergius process are discussed. Lab. tests carried out in a fixed autoclave with a residue from Borneo petroleum (h. above 300°), pitch from the same oil, and pitch from Mexican petroleum ( $d_{40} 1.0274$ ) are described in detail. They gave the following results: Pressure curves similar to those described by Bergius were obtained. The sp. gr. of the residue obtained in the Engler distn. test was lower with "berginized" oils than with cracked oils. With Borneo petroleum fraction, temp. was extremely important; optimum at 403-410°, 420° being too high (excessive amt. of cracking) and 388° too low (slight "berginization" owing to insufficient cracking). The temp. depends largely on the material used, the more easily cracked the lower the temp. of treatment. With Mexican petroleum pitch the optimum temp. was 385-390°. A. PAPINEAU-COUTURE

**The liquid fuel problem in its relation to the high-pressure hydrogenation process.** EDMOND CONNERADE. *Chimie et industrie Special No.*, 196-9 (May, 1923).—A discussion of the Bergius process. A. PAPINEAU-COUTURE

**The hydration of hydrocarbons.** PAUL WOOG. *Compt. rend.* 177, 60-2 (1923).—The absorption of water by hydrocarbons is studied by noting the change in the potential necessary to produce an elec. discharge. A higher potential is required for the dry oils. The affinity of the unsaturated hydrocarbons for water is especially marked. J. A. ALMQVIST

**Identification of non-cyclic saturated hydrocarbons in petroleum fractions.** H. GAULT. *Chimie et industrie Special No.*, 186-7 (May, 1923).—G. suggests chlorinating in presence of metallic Fe, choosing conditions so as to add 1 Cl atom at a time, sepg. and identifying the chlorinated derivs. by distn. Tertiary C atoms are more readily chlorinated than secondary, and the latter more readily than primary. The method is being investigated with synthetic non-cyclic hydrocarbons. A. PAPINEAU-COUTURE

**Identification of aliphatic hydrocarbons in fractions of petroleum.** H. GAULT. *Oil Eng. Finance* 2, 476 (1922); cf. preceding abstract.—A review. Bromination of C chains in the presence of Fe gives polybrominated substances varying according to the conditions of the expt., but equal to the number of atoms of C. The ease with which H can be substituted in a C chain depends upon phys. factors, chiefly temp. D. F. B.

**Production of liquid hydrocarbons from ethylene.** A. DAMERS. *Chimie et industrie Special No.*, 208 (May, 1923).—Heat CuO or Cu salt with H<sub>2</sub>SO<sub>4</sub> (or dissolve 5% of anhyd. CuSO<sub>4</sub>) and let cool. Absorb C<sub>2</sub>H<sub>4</sub> at ordinary temp. in the presence of metallic Hg or HgSO<sub>4</sub> (2%), with continuous agitation. The amt. of C<sub>2</sub>H<sub>4</sub> absorbed is about 100 times that absorbed by H<sub>2</sub>SO<sub>4</sub> alone. On letting stand a light slightly yellowish oily liquid seps. and a paste settles out. If a small quantity of the latter be immediately mixed with pure H<sub>2</sub>SO<sub>4</sub> the latter immediately acquires max. absorbing capacity. This activity of the catalyst rapidly decreases and is entirely gone in 24 hrs.

The oil produced is a mixt. of satd. hydrocarbons, d. 0.77, b. above 100°; compn. varies according to the b. p.

**The flash point of light liquid fuels.** W. R. ORMANDY AND E. C. CRAVEN. *Chimie et industrie Special No.*, 220-30 (May, 1923).—Results are given of a large no. of detns. made with O. and C.'s flash-point app. (C. A. 16, 1147). The ratio of the flash point to the b. p. (on abs. scale) is approx. const. and has a value of 0.738. Vapor tensions at the flash point are given, and the min., optimum and max. % for explosion mixts. are calcd. from Dalton's law. A pressure cup is shown for detg. flash points under high pressures, and curves are given for  $C_7H_8$  and 95% and abs. alc. at pressures up to 5000 mm. of Hg, and for  $C_7H_{16}$ , EtOH and  $C_7H_8$  in mixts. of O with N and  $CO_2$ , resp.

**An installation for heavy fuel oil.** W. C. BUELL. *Iron Age* 112, 129-32 (1923).—Details are given of the design and operation of oil-burning furnace equipment designed to avoid the high cost and limited supply of light fuel oil.

**The decomposition by heat of heavy petroleum products.** H. POULEUR. *Rev. universelle mines* 17, 215-32 (1923).—A review.

**Depolymerization of heavy hydrocarbons.** FRANÇOIS GAUDIN. *Chimie et industrie Special No.*, 209-11 (May, 1923).—A description of the Scigle process and app. (Fr. pat. Dec. 22, 1921) and of its performance in semi-com. tests. The material is introduced at about 300° into the still and the vapors produced are subdivided into thin sheets by disks carrying the catalyst (Cu, Fe, Al, Ni), the action of which raises the temp. to about 550°. The pressure does not exceed 0.015-0.020 m. of water. The mixed vapor and gas are sent to two or more coolers in series where the pressure is reduced. In the first one the cooling agent is  $CaCl_2$  soln. at 230°, intense cooling being effected by boiling of the water. The condensate from this cooler is returned to the still. Heavy gasoline, kerosene and lubricating oils condense in the second cooler at 100°, and the remaining vapors (light gasoline for automobile and airplane motors) are condensed in an ordinary condenser, the remaining gases being suitably collected. Heavy petroleum residues were depolymerized yielding 50-60% light distillate suitable for explosion motors, with a fuel consumption (for heating) of 49 l. to depolymerize 101 l. giving 50 l. of gasoline.

**Most any crude will make absorption oil.** H. PENNINGTON. *Refiner & Nat. Gasoline Mfr.* 2, No. 7, 9-11 (1923).—The essential requirements of good absorption oil (for making casinghead gasoline) are high initial b. p., relatively high gravity, absence of unsatd. hydrocarbons, low emulsification, and low cold test. The process of refining has more in general to do with the quality of the oil to be manufd. than the crude. Crudes high in paraffin will usually produce absorption oil of high cold test. The cold test should not be over 30° F. Methods of refining to get the desired properties are discussed.

**Evaluation of casinghead gas.** O. U. BRADLEY. *Trans. Am. Inst. Mining Met. Eng.* 1253-P, 14 pp. (1923).—Statistics are given graphically of the production of casinghead gasoline, av. productivity of the gas in gal. per 1000 cu. ft., av. price of the gas and the market price of the gasoline from 1921 wells in Oklahoma.

**Gasoline saved on government trucks by adjusting carburetors by exhaust gas analysis.** G. W. JONES AND A. C. FIELDNER. *Bur. Mines, Repts. Investigations No. 2487*, 13 pp. (1923).—The mixts. used by 10 government trucks employed in hauling coal were detd. by analysis of the exhaust gases. In every case excepting one, the mixt. was too rich. Change to a more economical mixt. was made by using the leanest mixt. possible without decreasing the max. power. Complete details of app. and methods of analysis are given. Adjustable carburetors deliver too rich a mixt. during use, and the setting by gas analysis should be made at intervals of two months or less. Increased mileage for each of the three months was 21.9, 16.2 and 8.9%.

**Transformation of solid or high-boiling point hydrocarbons into volatile liquid hydrocarbons.** A. MAILHE. *Chimie et industrie Special No.*, 188-95 (May, 1923).—Review of cracking, pyrogenic reactions (production of aromatic hydrocarbons), catalytic decompn. and  $AlCl_3$  process.

**The method of working the Burton cracking process.** A. FABER. *Petroleum Z.* 19, 643-8 (1923).—The Burton process is described and its development is reviewed.

**The Dubbs cracking process.** GUSTAV EGLOFF. *Chem. Age (N. Y.)* 31, 309-11 (1923).

**Some advantages of the Dubbs cracking process.** E. R. LEDERER AND W. F. FULTON. *Ref. & Nat. Gasoline Mfr.* 2, No. 2, 6-7 (1923).—A brief description with diagram of the process is given. Oil passes through a pipe still and into an expansion

chamber. Two vapor lines lead from the latter to the dephlegmator from which the vapors pass through the condenser and into the receiving drum, the whole system being maintained under about 120 lbs. pressure. Reflux from the dephlegmator and residuum from the expansion chamber are recycled through the app. until the gravity of the residuum has reached 20-22° Bé. Data are given on several runs made with North La. fuel oil and Mexican gas oil.

D. F. BROWN

**The French shale industry.** M. CAMBRAY. *Oil Eng. Finance* **2**, 477(1922).—General information of bituminous shales and their mineral and org. constituents is given. C. discusses the French shale industry as to retorts used, methods of distn., (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> manuf., refining of shale oils, plants, characteristics of the products and their uses and present and future prospects for the industry in France.

D. F. B.

**The development of oil shales and torbanites.** E. H. CUNNINGHAM-CRAIG. *Oil Eng. Finance* **2**, 478-82(1922).—Oil shale is an absorption product due to the so-called argillaceous deposits of petroleum formed in adjacent parent oil fields. Torbanites are essentially products of the carbonaceous phase and are, broadly speaking, a special form of cained coal developed *in situ*. Their advantages over oil shale are: (1) they yield their oil at a lower temp.; (2) they give a higher yield (80-100 gal. per ton for some French torbanites); (3) the oil is of better quality, costs less to refine, has less refining loss and gives more valuable refined products. Examn. has shown that torbanites are gels formed *in situ* by a combination of petroleum as it forms in minute globules with colloidal mineral matter in the beds. In contrast, the oil shale is a deposit which has absorbed and held oil obtained from elsewhere, losing a portion of the lighter and more valuable oils, but relatively gaining in the content of nitrogenous compds. A torbanite, on the other hand, is a petroleum deposit formed *in situ*, very rich in all forms of oil, and so much so as possibly to make it uneconomic to ext. the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. A discussion of the occurrence of shale deposits, prospects of exploitation and methods of retorting is given.

D. F. B.

**The bituminous limestones of Syria.** M. O. VEYRIER. *Oil Eng. Finance* **2**, 478(1922).—Ten beds of bituminous limestones have been proven and their positions registered in this region. During the war the Germans produced a heavy oil by the incomplete combustion of this mineral. A very viscous lubricant was obtained. Analysis shows that there is from 5 to 22% of oil in this rock. The powd. mineral can be burned in specially constructed furnaces and it can be distd. without the use of other fuel. The distillate is identical with petroleum, contg. light fractions coming over below 100°. The residue of the combustion of the limestone is lime having hydraulic qualities. The limestone fuel could be used in special furnaces for the production of bricks, tile and plaster.

D. F. B.

**Ointment-like machine fats.** H. MAYER. *Seifensieder Ztg.* **50**, 301(1923).—A description of the manuf. of lubricating greases of smooth ointment consistency, made of a lime soap dissolved in mineral oil of 0.875-0.900 sp. gr. These greases have a "drop"-point of 70-97°.

P. ESCHER

**Oil shales. II. Fuel shales and shale oil recovery in Esthonia.** E. RINNE. *Petroleum Z.* **18**, 1441-4(1922).—A general review of the shale deposits of Esthonia giving analyses of various samples and of the shale oils distd. therefrom.

D. F. BROWN

**The asphaltic mines of Ragusa.** GAETANO CASARELLI. *Russ. min. met. chim.* **53**, 136-41(1923).—An illustrated description of the production of asphaltic materials at Ragusa. The asphalt occurs in miocene limestone and is the richest hydrocarbon deposit in Sicily. The base of the calcareous mass is composed of compact rock suitable for the production of lime, and above is a zone of soft limestone in which occur bituminous impregnations. The exploitable area is over 100 hectares and the utilizable limestone is approx. 75 m. thick and contains several hundred million tons. The asphaltic mineral is sepd. from non-asphaltic material and divided in 3 grades, contg. 10, 8 and 6% bitumen, resp. The 10% grade is used for sizing, the 8% grade for railways and the 6% grade and any waste are consumed in gasogens for the production of mineral oils. Analysis of various samples showed varying results, with the following av. %: sol. bitumens 9.24, SiO<sub>2</sub> 0.59, Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub> 0.33, MgCO<sub>3</sub> 0.72, CaCO<sub>3</sub> 87.98, H<sub>2</sub>O 0.96, residue 0.18. The most important use of the asphaltic mineral is for the recovery of mineral oils. The gasogens consist of vertical ovens 16 m. high in batteries of 16 units. They are charged at the top, at which place the gases escape, and the exhausted material is removed intermittently at the bottom. The vertical section has a slight constriction at the middle to localize better the zone of combustion. In this zone, by means of injected air, part of the combustible material burns and the product in the form of vapor, chiefly N, CO<sub>2</sub> and gaseous oils, passes through a bed of recently charged rock and cools to approx. 50°. Only a very small amt. of hydrocarbons is deposited in the mass,

and the oil, which is suspended as globules in the gas, is distd. and condensed. The crude oil from the gasogens is a uniform brown liquid, with empyreumatic odor, d. 0.963, of approx. 10,000 cals., liberating small fractions below 300° and leaving on distn. a bituminous residue of approx. 15%. It is used in large amts. in Diesel engines. The main constituents are asphaltic oils, b. 300–60°, and are superior to ordinary mineral oils for lubrication. Concd. by further distn. they give an excellent lubricant for heavy machinery, such as locomotives. By refining the crude oil, lubricating oils with d. at 50° of 5, 10 and 20° (Engler), resp., are produced. C. C. DAVIS

**Manufacture of asphalt.** I. K. GILES. *Oil News* 11, No. 14, 28, 44 (1923).—A general review dealing chiefly with the physical properties of typical manufd. asphalts. D. P. BROWN

**Heat treatment of hydrocarbon oils.** L. H. MANNING. U. S. 1,462,068, July 17. Hydrocarbon oils are cracked in externally heated retort tubes in which the oil is continuously agitated by rotating vanes and steel balls. U. S. 1,462,069 relates to an app. for carrying out this process.

**Cracking hydrocarbon oils.** F. T. MANLEY. U. S. 1,462,143, July 17. Oil to be cracked is charged into a vertical still of considerable height in which a long column of liquid oil is maintained at a temp. and pressure which will effect cracking. Residuum and vapors are removed from the still so as to maintain a practically const. level in the still and heavy constituents are sepd. from the vapors and forced into the column of liquid near the bottom of the still for retreatment. Cf. C. A. 16, 3753.

**Cracking hydrocarbon oils.** W. F. RITTMAN. U. S. 1,462,247, July 17. A relatively large liquid mass of hydrocarbon oil is cracked under pressure, the desired end product is sepd. and the residue of the products is vaporized and the vapors are cracked by heat and pressure to obtain additional amts. of the end product desired. Cf. C. A. 16, 2778.

**Cracking hydrocarbon oils.** J. H. ADAMS. U. S. 1,462,677, July 24. Oil from a supply tank is forced to one end of a plurality of vertical converter tubes and passed through the tubes to be cracked. Cracking temp. and superatm. pressure are maintained between the ends of the tubes and unconverted liquid oil is withdrawn from the opposite ends of the vertical converter tubes and returned to mix with oil from the supply tank for retreatment. C and heavy residuum are withdrawn from the lower portion of the converter tubes and vaporized products are led off to a condenser. The oil may be preheated under pressure before introduction into the cracking tubes. U. S. 1,462, 678 relates to app. for carrying out similar processes. Cf. C. A. 17, 466, 2360.

**Cracking hydrocarbons.** G. F. FORWOOD and J. G. TAPLAY. Brit. 190,284, Oct. 7, 1921. In cracking and hydrogenating hydrocarbon oils by passing their vapors together with steam over heated C derived from shale, wood, peat or other vegetable or animal matter, the gases from the condenser are freed from H<sub>2</sub>S, and preferably also from CO<sub>2</sub>, and passed together with oil vapors and steam through the retort. CO<sub>2</sub> may be removed by passage through slaked lime, and H<sub>2</sub>S by means of hydrated oxide of Fe. Vapors from high-boiling oils and those from low-boiling oils are passed alternately through the retort, so that C deposited from the high-boiling oils is used up during treatment of low-boiling oils.

**Purifying and distilling hydrocarbons.** W. DEDERICH. Brit. 191,037, Dec. 22, 1922. Crude petroleum or other hydrocarbon is heated with soaps of Na, Fe, alk. earth, or other metal, whereby at 100–10° or over the hydrocarbon is desulfurized, and on distn. the fractions are clean and sharp. A catalyzer, such as 0.5% of NaOH or a few drops of H<sub>2</sub>O, is preferably added. The desulfurization of hydrocarbon oils, by (1) heating crude petroleum or other oil with small pieces of FeS, (2) passing the vapors of petroleum distillates through a soln. of metal soaps, or (3) acidifying a cold mixt. of burning oil and metal soap dissolved in burning oil distillates so as to ppt. the metal of the soap, and afterwards neutralizing by alkali, is also described.

**Checker-work furnace for oil stills.** P. HEFFLER. U. S. 1,463,698, July 31.

**Retort for distillation of oil-shale.** W. M. STRONG. U. S. 1,462,023, July 17.

**Apparatus for continuous scrubbing or purification of gasoline.** T. A. GROSS. U. S. 1,462,335, July 17.

**Aluminium chloride from oil-refining residues.** R. HADDAN. Brit. 191,582, Dec. 12, 1921. AlCl<sub>3</sub> is recovered in substantial amt. without the use of Cl by distg. the hydrocarbon residues obtained in processes for the treatment of oils with AlCl<sub>3</sub>. Free hydrocarbons are first removed and condensed and on raising the temp., preferably to 1450° F., AlCl<sub>3</sub> is evolved. By treatment with Cl or HCl gas a further quantity of AlCl<sub>3</sub> may be obtained. The yield is increased by adding, preferably after the re-

removal of the hydrocarbons, a small quantity of Al or an Al compd. such as the carbide or sulfide. Cl compds. which may be evolved during the heat treatment may also be conserved by passing them, together with the  $\text{AlCl}_3$ , over aluminous material before they enter the condensers. A suitable construction is evolved.

**Preventing emulsification of oil discharged from wells.** R. G. JONES. U. S. 1,462,748, July 24. A mixt. of oil,  $\text{H}_2\text{O}$  and gas at a well discharge pressure is introduced into a column of oil and  $\text{H}_2\text{O}$  under a less pressure (and under superatm. pressure) beneath its surface and gas is discharged from the space above the column as it rises. Oil and  $\text{H}_2\text{O}$  are led at different levels into other columns and are discharged.

**Lubricant.** J. A. BURTON. U. S. 1,462,799, July 24. A lubricant suitable for use on leaf springs is formed of crude petroleum 3 qts., kerosene 18 oz., graphite 6 oz., ethyl ether 7 oz.,  $\text{AmOAc}$  3 drams,  $\text{EtOAc}$  3 drams,  $\text{Et}$  butyrate 2 drams and oil of cassia 5 minims.

**Lubricant.** R. G. PELLY. U. S. 1,463,092, July 24. Lubricating oils such as mineral oils are mixed with 5% of derivs. of aliphatic polyhydric alcs. in which the OH groups are replaced by acid radicals, e. g., mono- or di-glycerides of oleic acid, lauric acid or stearic acid.

## 23—CELLULOSE AND PAPER

CARLETON E. CURRAN

**Chemistry of wood cellulose. II. Nature of wood cellulose.** L. E. WISE. *Ind. Eng. Chem.* 15, 711-3(1923).—A critical summary is given of the exptl. work of various investigators with the formulation of a working hypothesis on the nature of wood cellulose. No new exptl. data are included. Wood cellulose, like cotton cellulose, is believed to be an aggregate of comparatively small units held together by secondary valence. Most of the units appear to be identical with those of cotton cellulose, but the presence of other units, like those of the pentosans, mannans, or any other polysaccharide is not excluded, since they may be elaborated and adsorbed during the growth of the cell. **III. The acetolysis reaction applied to cellulose isolated from commercial species of wood.** L. E. WISE AND W. C. RUSSELL. *Ind. Eng. Chem.* 15, 815-8(1923).—Acetolysis of  $\alpha$ -celluloses isolated from 10 com. woods under carefully controlled conditions yielded appreciable amts. of cellobiose octaacetate from all, varying from 24 to 33% of the theoretical yield. Fiber silk (from spruce) gave 24% octaacetate and normal cellulose from cotton and Southern pine (prepd. by the sulfate process) yielded 34 and 33% cellobiose octaacetate, resp. The cellobiose grouping appears to be present in all of the celluloses examd. An appendix by E. T. WHERRY gives the optical properties of the octaacetate and means of identifying the compd. LOUIS E. WISE

**Gelatinization of lignocellulose.** I. A. W. SCHORGER. *Ind. Eng. Chem.* 15, 812-4(1923).—Whereas coniferous woods in general may be readily gelatinized by grinding with  $\text{H}_2\text{O}$ , hardwoods are not subject to much change by this treatment. Marked peptization of hardwoods was noted when the latter were ground with aq.  $\text{NaOH}$ , and the resulting gelatinized lignocellulose gave a hard horn-like mass on drying. In general the hardwoods are more readily affected by grinding with alkali than are the conifers. LOUIS E. WISE

**Key industry of the South (of the United States).** H. W. HOLCOMBE. *Paper* 32, No. 10, 13-4(1923).—An exptl. plant at Hattiesburg, Miss., has successfully treated yellow-pine stumps for the extn. of naval stores and treatment of the residue for the manuf. of kraft pulp. A new type of cooker-drum allows of the application of steam immediately to every particle of the wood, reducing the time of distn. one-third. A new solvent is used and is entirely recovered. Improved hogging, rolling and crushing methods leave the residue in excellent shape for transformation into paper pulp, which, it is expected, can be bleached. A. PAPINEAU-COUTURE

**Limestone tower installation.** ANON. *Paper Trade J.* 77, No. 3, 48(1923).—A description of the first Jenssen tower installation in Germany built at the Ashaffenburg mill of A. G. Zellstoff und Papierfabrikation. A. PAPINEAU-COUTURE

**Parchment and imitation parchment.** H. POSTL. *Paper* 32, No. 10, 11-2(1923).—Brief sketch of the manuf. of vegetable parchment and of its substitutes. A. P.-C.

**Weighing wood in the manufacture of pulp.** B. S. SUMMERS. *Paper Trade J.* 77, No. 2, 55-7(1923).—The advantages of weighing wood are: indication of the quality of the wood; location of the chief losses in manuf. as between depts.; stimulation of research and efficiency of management to save losses. Dctn. of barking loss and weighing of chips to get bone-dry wt. (in actual mill operations) resulted in an increase in the

yields of screened pulp from 45% to 53%, and of total pulp from 47-8% to 56%, while the purity, color and quality of the pulp were improved. A pulp contg. 94-6% cellulose, about 2% lignin, and requiring 12-6% of bleach, was obtained. A. P.-C.

**The cooking of sulfite pulp.** M. L. GRIFFIN. *Paper Mill* 47, No. 27, 4, 8(1923).—A criticism of modern cooking methods from the standpoint of circulation. The Tompkins system is considered superior to the Morterud system; the advantages of the former are discussed. A. PAPINEAU-COUTURE

**Sulfur consumption in the manufacture of sulfite pulp.** W. G. MACNAUGHTON. *Paper Mill* 47, No. 29, 30(1923); *Pulp Paper Mag. Can.* 21, 780(1923).—Brief discussion of the factors affecting S consumption. A. PAPINEAU-COUTURE

**Utilization of sulfite-liquor. With an explanation of the Strehlenert process.** K. MORCH. *Tidsskrift for Kemi og Bergvaesen* 3, 44-8(1923).—In his own plant M. uses 3 lead-lined autoclaves in succession, in combination with a preheating system. The liquid from the boilers is pumped by 20 atm. pressure through the preheater and next into the bottom of the first vessel, where air and some direct steam are also applied. From the top of the vessel the mixt. of air and liquor is conducted into the bottom of the second autoclave and so on. From the top of the third vessel the mixt. of air and gases is let out, while the liquor goes to the preheating system to give off some of its heat to the untreated liquor and finally into sedimentation vessels where the lignites sink to the bottom. After decantation a substance with about 50% of dry matter is obtained, which can easily be burned. The content of dry matter in the mother liquor can be worked down to about 3% by this procedure. CHV. H. A. SVERTSEN

**The manufacture of pulp and paper from Australian woods.** L. R. BENJAMIN. *Australian Inst. Sci. Ind. Bull.* 25(1923); cf. C. A. 17, 4062.—Pulping and paper-making trials were made on the more abundant forest species on lab. and semi-com. scales. All cooks were made by the soda process. Semi-com. cooks were varied from standard practice in that the cooking liquor was heated externally and lower concns. of Na<sub>2</sub>O (30-40 g. per l.) were used. Cooking pressures were 80-100 lbs. per sq. in. Cooking time was 5-6 hrs. at max. pressure. With 20-35 lbs. of alkali per 100 lbs. bone-dry wood in the above concns. the wood could be kept covered at all times in the cook, thus producing higher yields of easily bleaching pulp (45-50% bone-dry) in shorter time. By modifying the beating process exceptionally strong papers were obtained in spite of shortness of fiber. With a mixt. of 60% pulp from local species with 30% imported spruce sulfite and 10% waste paper a good paper of fairly wide range of uses was obtained. The following species of *Eucalyptus* in the young re-growth condition are suitable for paper-making material: *E. pilularis* (Blackbutt), *E. dalympiana* (Mountain Gum), *E. maculata* (Spotted Gum), *E. regnans* (Mountain Ash, Gum-top), *E. delegatensis* (Woodybutt, Gum-top), *E. sieberiana* (Silvertop, Coast Ash), *E. diversicolor* (Karri), *E. marginata* (Jarrah), *E. calophylla* (Red Gum, Marri), *E. obliqua* (Stringybark, Messmate), *E. globulus* (Blue Gum). The sulfate process is suggested for the following species: *Aleuries moluccana* (Candlenut), *Tarrietia argyrodendron* (Crow's foot Elm), *Grevillea robusta* (Silky Oak), and *Callistris glauca* (Swamp Cypress). The eucalypts seem to offer the most important field for immediate exploitation. Evidence is presented showing that a domestic pulp and paper industry would be an economic advantage. W. H. SWANSON

**Seed flax straw as paper-making material.** E. H. KELLOGG, M. B. SHAW AND G. W. BICKING. *Paper Trade J.* 77, No. 5, 43-9(1923).—Lab. and com. expts. carried out by the sulfate process are described in detail; they led to the following conclusions. Fair quality of wrapping paper can be made from whole seed flax straw, and good quality wrapping from seed flax tow, provided special care is taken to eliminate specks. Pulp from the tow can be readily bleached. The consumption of chemicals using whole straw is about double that for wood, and with tow only slightly greater than for wood. A modified sulfate process using equal parts of NaOH and Na<sub>2</sub>S did not give satisfactory results. At present it is not economically feasible to use seed flax fiber for making paper of any description by the sulfate process. A bibliography is given. A. PAPINEAU-COUTURE

**The saccharification of cellulose.** B. P. BUDNIKOV. *Z. angew. Chem.* 36, 328-8(1923).—Glucose may be obtained as the chief product of the hydrolysis of cellulose by treatment of the latter with cold concd. H<sub>2</sub>SO<sub>4</sub>, dig. the clear soln. with H<sub>2</sub>O, and heating. Previous experimenters have only prepd. dil. solns. (0.6%) of glucose and have used excessive amts. of acid. B. describes expts. in which glucose solns. of higher concn. may be prepd. and the acid destroyed by the addition of BaCO<sub>3</sub>. One g. dried Swedish filter paper was dissolved in 7-8 cc. 72% H<sub>2</sub>SO<sub>4</sub>. After 3 hrs. a clear soln. was obtained; this was dild. with H<sub>2</sub>O to 3% H<sub>2</sub>SO<sub>4</sub> content and heated for 2 hrs. in an



autoclave at 120°. A soln. of approx. 0.4% strength was obtained; the  $\text{H}_2\text{SO}_4$  was removed by pptn. with  $\text{BaCO}_3$ . The second 1-g. sample of filter paper after treatment with  $\text{H}_2\text{SO}_4$  was dild. with the first glucose soln. instead of with  $\text{H}_2\text{O}$ . By dild. the third sample with the glucose soln. from the second sample its strength was increased. This method was continued until the seventh sample contained 1.656 g. glucose per 100 cc.

C. T. WHITE

**New theories on rosin sizing.** EMIL HEUSER. *Swensk Pappers-Tid.* 26, 114-5, 202-5(1923).—H. reviews the theories of Illig and Wurster and points out their deficiencies. According to his own theory cellulose acts as a negatively charged colloid and adsorbs the positively charged colloidal  $\text{Al}(\text{OH})_3$  present in a soln. of alum from hydrolysis. Sodium resinate is hydrolyzed in soln. and produces a negatively charged colloidal resin acid. A colloidal sodium-free resin acid soln. will not size paper until a soln. of alum is added or a colloidal soln. of  $\text{Al}(\text{OH})_3$ . The ppt. formed has sizing properties. If the colloidal resin acid is pptd. by  $\text{NaHSO}_4$  or  $\text{MgSO}_4$ , it has no sizing properties. Sizing proceeds when the  $\text{Al}(\text{OH})_3$  is replaced by  $\text{Fe}(\text{OH})_3$  or  $\text{Cr}(\text{OH})_3$  and is termed electrolytic coagulation. The first stage of sizing is the production of a positively charged coagulated substance from the resin acid soln. and the  $\text{Al}(\text{OH})_3$  soln. The second stage is the adsorption of this substance on the negatively charged cellulose. The third stage takes place on the dryers of the paper machine at a temp. of 70-80° by a sintering process, before the moisture content of the paper falls below 50%.

FRANCIS G. RAWLING

**Products obtained in the hydrolysis of white spruce wood with dilute sulfuric acid under steam pressure.** E. C. SHERRARD AND G. W. BLANCO. *Ind. Eng. Chem.* 15, 611-6(1923).—Optimum cooking conditions were found to be 115 lbs. pressure for 15 min., with 2.5 parts  $\text{H}_2\text{SO}_4$  (100%) per 100 parts of dry wood and 2 parts  $\text{H}_2\text{O}$  for every unit wt. of wood. The products obtained from white spruce were 1.9% volatile acids, mannose, glucose, galactose, xylose and arabinose, glucose and mannose predominating. Wood residues after hydrolysis show a greatly decreased yield of  $\text{AcOH}$  and pentosans, an appreciable decrease in cellulose, but no marked change in lignin content. A loss in  $\text{MeO}$  was also noted. Hydrolysis of wood decreases  $\alpha$ - and  $\gamma$ -cellulose but increases  $\beta$ -cellulose. Hydrolysis of white spruce cellulose showed the presence of mannose even in the products from bleached cellulose. The ratio of yields of glucose to mannose was 3:1. Differences between constitution of wood and cotton celluloses are discussed.

LOUIS E. WISE

Carbon catalyst (from waste soda pulp liquor) (U. S. pat. 1,462,752) 18.

**Manufacture of cellulose.** E. SCHMIDT. Brit. 191,357, Feb. 14, 1922. Wood or the like is treated with  $\text{ClO}_2$  in solvents, such as dil.  $\text{HOAc}$ , which dissolve the lignin after it has been transformed by the  $\text{ClO}_2$ .

**Plastic cellulose ester compositions.** A. D. ST. JOHN. U. S. 1,462,306, July 17. A mixed cresyl phenyl phosphate, liquid at ordinary temp. and boiling at about 400° with but slight decompn. is used as a plasticizing agent with nitric or other cellulose esters.

**Paper pulp.** B. J. BELLINGER. U. S. 1,463,000, July 24. Chipped wood is digested and then subjected directly to carding to sep. the fibers.

**Paper.** F. KAYE. Brit. 191,446, Oct. 8, 1921. Addn. to 167,935 (C. A. 16, 342). A small quantity of a sol. alkali sulfide is added to rubber latex before the latter is dild. and mixed with paper pulp in the process described in the principal patent. On addn. of acid to coagulate the latex S is deposited for the subsequent vulcanization. With acid fibers, or paper sized with resin and alum, the addn. of acid may be unnecessary. Sufficient sulfide to produce 1-2% S calcd. on the rubber content is usually enough, but quantities to produce 10% may be added.

## 24--EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

**The freezing point-solubility diagram of the system TNT-picric acid.** C. A. TAYLOR AND W. H. RINKENBACH. *Ind. Eng. Chem.* 15, 795(1923).—M. ps. were detd. for 9 mixts. and each of the simple components and an equil. diagram were constructed from these data. The system proved to be a very simple one, no mol. compds. being formed. The eutectic temp. was 59.4°. The data may be utilized for analytical purposes as previously shown for the system TNT-tetryl (C. A. 17, 1331). C. E. M.

**The propagation of flame from a spark in a closed tube through a homogeneous inflammable mixture.** O. C. DE C. ELLIS. *J. Chem. Soc.* **123**, 1435-52 (1923).—The progress of flame through an inflammable mixt. was studied, by photographing it on a moving film, as it was propagated from a spark near the closed end of a tube, the other, or "distal" end of which was open. Such a tube may be regarded as a closed tube of infinite length. Opening or closing the firing end alters the mode of inflammation. The investigation covered observations on the firing cylinder, turbulence, the spark and the temp., and the pressure. The movement of the flame in any given mixt. depends on the length and bore of the tube, the position of the spark-gap, the initial mechanical turbulence, the intensity of the spark and the initial temp. and pressure. With central ignition the propagation is symmetrical, diverging flame-points approaching opposite ends of the tube, each giving a photographic analysis which is the mirror image of that of the other. Asymmetry is obtained, even with central ignition, if the spark gap does not mark an exact balance of vol. as well as of length. If ignition is not central the flame front approaching the nearer end will be slower than the other. The several movements of the flame are all slower the wider the bore of tube, when this is the only variable. Also the period between ignition and the setting up of the detonation wave, when the charge is fired near a closed end, will be greater, within limits, the wider the bore. Through defect in the sparking app. it was discovered that increase in speed due to turbulence is greater, *ceteris paribus*, for a weak spark. The  $C_2H_2$  mixt., which is the fastest of all, showed the least change in speed from turbulence. When a mixt. was fired under great initial pressure a mass of gas through which the flame has already passed becomes reignited, to a small extent, by a subsequent spark.

CHARLES E. MUNROE

**The measurement of flame velocity.** WALTER MASON. *Fuel* **2**, 110-4 (1923).—Illustrated directions are given of approved methods (*C. A.* **15**, 754) for measuring flame velocity in mixts. of gaseous fuels and air.

C. C. DAVIS

**Disastrous inflammation of coal dust in excavating a mine dump.** C. A. HERRERT. *Bur. of Mines, Repts. of Investigations No. 2498*, 2 pp. (1923).—At mines in the S. E. part of Ga. the fine coal and roof rock from the roadways are taken from the mine and piled in dumps on the surface where they take fire spontaneously and the "rock," which is a black oily shale, burns to a material which is excellent for road building and railway ballast. In removing it with steam shovel slides have formed through which recently dumped coal dust has been thrown up as a cloud and ignited, producing serious casualties. It is advised that a dump be wet down by spraying for several days before it is disturbed.

CHARLES E. MUNROE

**Explosives.** H. RATHSBURG. *Brit.* **190,215**, Sept. 10, 1921. A priming compn. for loading blasting caps, Flobert ammunition, and the like consists of the Pb salt of trinitrophloroglucinol pptd. by allowing hot solns. of readily sol. salts to run together. One or two other substances may be pptd. simultaneously therewith, *e. g.*, a mixt. of solns. of the Na deriv. of trinitrophloroglucinol,  $NaN_3$ , and the Na salt of dinitrodinitrosobenzene may be run into a mixt. of a soln. of  $Pb(OAc)_2$  and  $KOAc$ . The blasting cap, etc., may also contain a top charge of another substance over the charge of the Pb deriv. of trinitrophloroglucinol. The following substances are mentioned for use in conjunction with the Pb salt of trinitrophloroglucinol: the salts of trinitrodinitroso- $\beta$ -naphthol, difficultly sol. salts of tetrazole and its derivs. such as tetrazylazoimide, azo-, hydroxyazo-, diazoamide-, diazotetrazole, bistetrazole, azotetrazolate of Pb, heavy metal salts of diazoaminotetrazole such as those of Pb, Cu and Cd, substituted dihydroxytetrazole,  $PbN_3$ , and Pb derivs. of di- and tri-nitroresorcinol.

**Desensitized explosive.** W. H. WARD. U. S. 1,462,753, July 24. A desensitized explosive adapted for use in drop bombs and trench mortar shells is prepd. from nitrated starch 40-5, an inorg. nitrate such as  $NaNO_3$  32-40,  $H_2O$  10-5 and heavy lubricating petroleum oil 0-5 parts.

**Detonator composition.** C. E. WALLER. U. S. 1,462,093, July 17. Primer compns. are formed of nitrostarch in granules of an av. size in excess of 0.045 mm. together with oxidizing and stabilizing agents such as  $KClO_3$  and diphenylamine.

**Detonator.** W. O. SNELLING. U. S. 1,462,074, July 17. Detonators are formed with an initial priming charge of Hg fulminate mixt. or a similarly acting material, and a main charge contg. nitrostarch together with an oxidizing agent, *e. g.*,  $KClO_3$ , and a stabilizing agent such as diphenylamine. U. S. 1,462,075 relates also to detonator compns. contg. nitrostarch and  $KClO_3$  or other oxidizing agent, with or without diphenylamine.

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

**The nature of the changes occurring in the indigo steeping vat. II.** W. A. DAVIS. Agr. Research Inst. Pusa, *Indigo publication* 11, 81 pp.(1922); cf. C. A. 16, 649.—Steeping trials were made in sterilized water with indican-splitting bacteria. Fermentation was stopped when destructive changes began. With heavy loading (100 mounds per 1000 cu. ft.) the efficiency of extn. was about 85% with plants of poor quality and decreased as the quality increased. The extn. was about 0.5 g. indigotin per l. of vat liquor and was independent of plant quality. With light loading (80 mounds plant) the extn. efficiency was high and practically const. at 80 to 85%, and independent of plant quality between the limits 10 to 18.5 seers indigotin per 100 mounds. Concn. of indoxyl in vat liquor varied with quality up to 0.5 g. indigotin per l. The purity of the indigo is proportional to the plant quality, showing more variation with the lighter loads. The optimum time for extn. (12 to 13 hrs. at 90° F.) depends on the kind of bacteria causing fermentation and not on the loading or quality. The concn. of ext. at the bottom of the vat is nearly double that at the top. Acidity, behavior towards oxidation, etc., show a similar variation. Efficiency was greater during the rains than before. The quality of indigo varied with the efficiency of working. Liming the vats caused increased efficiency and purity. The time control test is most useful before the rains when efficiency and purity are low. Plants cut before the rains vary greatly in quality and should be loaded lightly. With heavy loading, increasing the amt. of inoculum increases the extn. Under similar steeping conditions the purity of the indigo is proportional to the quality and nature of the fermentation.

HENRY W. EASTERWOOD

**Wood.** FRIEDRICH ZIMMERMANN. *Textilber.* 4, 330-2(1923).—Historical sketch of the culture and use in dyeing of wood.

E. R. CLARK

**Practical experiences in the fast dyeing of half-woolens.** FRANZ POLLEY. *Z. ges. Textilind.* 25, 267-8; *Chem. Zentr.* 1922, IV, 318.—The preliminary dyeing of cotton and linen fibers, mordanting with  $K_2Cr_2O_7$  and tartar with the addn. of  $CuSO_4$ , the dyeing of cotton with alizarin dyes, the preliminary dyeing of cotton and redyeing with developing dyes are described. A list of suitable dyes is included.

C. C. DAVIS

**Sizings applicable to calico printing from the point of view of colloid chemistry and their influence on the dyeing of lakes formed on the fibers in connection with the process of calico printing.** N. J. PLANOWSKY. *Ber. Polytechnikum Iwanowo-Wosniessensk* 4, 129-37(1921); *Chem. Zentr.* 1922, IV, 551-2.—The most frequently used natural sizings, such as starch, dextrin, British gum, gommelin, and leigum, were studied. Physically they are pseudo-solns., chemically they are colloids. Based on their compn. they are heterogeneous liquids, on the degree of dispersion of the suspension they are heterogeneous, homogeneous or micellar, but this classification is not wholly definite since the various types may pass over into the others on standing. Several of the sizings examd. were electrically charged colloids. A starch soln. gives a ppt. with tannin so that in printing with basic dyes only a print by pptn. occurs. Such a lake adheres only superficially and therefore is not permanent. British gum and gommelin give similar ppts. due to starch contained as an impurity. Starch is the strongest colloid, gommelin the weakest. This is of importance in printing. With starch and gum tragacanth there is partial diffusion of the dyestuff, during printing, into the thread. This is accelerated by steaming. The diffusion is very slight in homogeneous sizings and the steam does not increase it; therefore such lakes are not fast to washing and are not colored strongly. Prints with malachite green were found to be deepest with starch and gum tragacanth, much weaker with gommelin and British gum. Simultaneous diffusion expts. showed that gum tragacanth possessed the strongest and British gum the weakest diffusion capacity.

C. C. DAVIS

**Felting of textile fibers.** WILHELM MANG. *Textilber.* 4, 326-8(1923).—Photomicrographs show that the felting of wool, etc., is caused by the fibers being bent back on themselves and hooked together.

E. R. CLARK

**Differentiation between varieties of cotton.** R. MALLER. *Textilber.* 4, 325-6(1923).—Microscopic study of the seed and leaf particles in raw cotton serves to identify the fiber geographically. Insufficient data are reproduced to make duplication of the method possible.

E. R. CLARK

**Artificial silk.** ARTHUR FATH. *Chem. Age (N. Y.)* 31, 245-8, 300-2(1923).—A description of the manuf. of artificial silk from viscose.

E. H.

**From raw wool to pure wool.** A. GANSWINDT. *Monatschr. Textilind.* 37, 223-7

(1922); *Chimie et industrie* 9, 1201 (1923).—The wool-scouring process is described, and a plea is made for evolving a process which will allow of more complete recovery of by-products. A. PAPINEAU-COUTURE

**Dyes.** SOC. ANON. POUR L'IND. CHIM. A BAIE. Brit. 191,305, Feb. 16, 1922. Monoazo dyes, yielding fast violet-blue to brown shades when chrome printed on cotton, are obtained by coupling diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid, or a substitution product thereof, with  $\beta$ -resorcylic acid; in examples the diazo compd. itself and the nitrated diazo compd. are used.

**Dyes from 1-mercapto-2-aminoanthraquinone.** P. KACER. U. S. 1,459,536, June 19. 1-Mercapto-2-aminoanthraquinone or one of its derivs. is condensed with an aromatic compd. contg. as substituents at least 2 "reactive C atoms" such as are found in the COOH or aldehyde group or in halogenated alkyl or COCl groups, e. g., terephthalyl chloride. Dyes thus formed give violet hyposulfite vats which dye cotton yellow or orange yellow shades.

**Indigoid dyes.** H. STAUDINGER, H. VERGUTH and R. TOBLER. U. S. 1,461,435, July 10.  $\beta$ -Thionaphthisatin, m. 133° (obtainable from oxalyl chloride and  $\beta$ -thionaphthol), on reaction with cyclic compds. contg. methylene groups, e. g., indoxyls, thioindoxyls, pyrazolones, acenaphthenone,  $\alpha$ -oxanthracene,  $\alpha$ -naphthol or their derivs., forms indigoid dyes which are dark powders giving with alkali and hyposulfite orange-yellow to olive-green vats which dye wool and cotton solid red to brown to blue-black tints. Halogenization converts the dyes into products of a deeper or more "solid" color.

**Indigo dyeing.** MANSAKU IKEDA, YOSHICHIKA TAKATA and FUSAKICHI UMERU. Japan. 41,630, Jan. 31, 1922. Addn. to 36,870. The following mixts. are used: (1) A dyestuff 1.5 or 3 g., powdered indigo leaves 2 or 4 g., NaOH of 40° Twd. 30 or 45 cc., and NaHSO<sub>2</sub> 3 or 6 g.; total amt. of the soln. 600 cc. (2) A dyestuff 1.5 or 3 g., powdered leaves 2 or 4 g., NaOH of 40° Twd. 23 or 35 cc., NaHSO<sub>2</sub> 2.5 or 5 g., Na<sub>2</sub>S 0.5 or 1 g.; total amt. 600 cc. (3) A dyestuff 1 or 3 g., powdered leaves 1 or 3 g., NaOH of 40° Twd. 12 or 30 cc., and NaHSO<sub>2</sub> 2 or 5 g.; total amt. 600 cc.

**Indigo dyeing.** MANSAKU IKEDA, YOSHICHIKA TAKATA and FUSAKICHI UMERU. Japan. 41,631, Jan. 31, 1922. Addn. to 36,870. Leaves of indigo plants are steamed for 10–20 min., ground in a mortar or a beater with 3 parts of H<sub>2</sub>O and used for dyeing singly or with other dyes; the dyeing temp. is 60° and the time 30 min. The following mixts. are given as examples: (1) Indigo 1 or 4 g., ground leaves 1 or 4 g., NaOH of 40° Twd. 12 or 40 cc. and NaHSO<sub>2</sub> 2 or 6.5 g.; total amount of the liquor 600 cc. (2) A vat color 1.5 or 3 g., ground leaves 2 or 4 g., NaOH of 40° Twd. 30 or 40 cc. and NaHSO<sub>2</sub> 3 or 6 g.; total amt. 600 cc.

**Dyeing cellulose acetate.** R. CLAVEL. Brit. 191,553, Nov. 19, 1921. Cellulose acetate goods are dyed with vat or S dyes in hyposulfite vats kept weakly alk. by NH<sub>3</sub>, only sufficient caustic alkali being present to form the leuco compd; preferably salts such as Ba, Ca, or Mg chlorides, and protective colloids such as boiled-off liquor, gelatin, glucose, or starch, are added to the vats. Examples are given of dyeing with brom-indigo and Pyrogenindigo. Cf. 182,830 (C. A. 16, 4356).

**Dyeing artificial silk fabrics.** A. E. HUNTER. Brit. 191,120, Sept. 21, 1921. Two-color effects are obtained on lace and other fabrics composed partly of cellulose acetate artificial silk and partly of cellulose artificial silk, by dyeing the acetate portion by means of a basic dye contg. amino or alkyl- or aryl-amino groups which have been liberated by treatment of the dye salt with Na<sub>2</sub>CO<sub>3</sub> or other suitable alkali, and previously, simultaneously, or subsequently dyeing the cellulose portion another shade by means of a direct cotton dye. Liberation of the dye base increases the affinity of the dye for the acetate silk while diminishing its affinity for the cellulose silk. The provisional specification describes also the dyeing of acetate silk with dyes contg. free amino groups.

**Ferrocyanides from waste dye liquors.** SILVER SPRINGS BLEACHING & DYEING CO., LTD. AND A. J. HALL. Brit. 191,687, July 21, 1922. The waste liquor from aniline black dyeing in which ferrocyanide is used is treated with FeSO<sub>4</sub> so as to obtain a blue ppt. as described in the parent case, and the blue ppt. is sepd. and dissolved by means of an alkali, alk. earth, or NH<sub>3</sub>. The Fe hydroxide also produced is sepd. from the soln. and the ferrocyanide is obtained by crystn. from the filtrate. Cf. 3,072, 1889 and 188,208 (C. A. 17, 1154).

**Finishing yarns and fabrics.** HEBERLEIN & CO., AKT.-GES. AND E. BEHRERLEIN. Brit. 191,203, Oct. 20, 1921. Addn. to 108,671 (C. A. 12, 96). The process described in the principal patent for imparting a transparent appearance to cotton yarns and

fabrics by treating the material with caustic alkali lye of over 26° Bé. and at a temp. below 0° is modified by subjecting the material to a group of lye treatments comprising a normal mercerization before or after or both before and after a treatment, or between two treatments, with the cold NaOH lye. Patterns are produced on cotton fabrics by printing them with reserves before or between lye treatments, the treatment with the cold lye following the printing with the reserve. The cotton may be treated with H<sub>2</sub>SO<sub>4</sub> of over 50.5° Bé., cooled or not, before or after a group of lye treatments, and reserves may be printed on cotton fabrics before an acid treatment or before a treatment with the cold lye. When the material is treated in the manner described in 100,483 (C. A. 10, 2409), a group of lye treatments is applied once or several times and H<sub>2</sub>SO<sub>4</sub> of over 50.5° Bé., cooled or not, is applied several times or only once, the material being stretched, if desired, during one or more of the treatments and one of the reagents being caused to react, if desired, only in places on the material.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

**Luminous paints and similar materials.** E. O. RASSER. *D. Opt. Wochenschr.* 8, 395-6, 412(1922); *Physik. Ber.* 3, 787(1922).—Certain recipes (already known) are given, and applications to the illumination of dark rooms and rendering visible of objects at night, are pointed out.

A. E. STEARN

**Submarine paints.** H. RABATÉ. *Rev. chim. ind.* 32, 106-11, 131-6, 159-60 (1923).—A discussion of the anti-corrosion and anti-fouling properties required of such paints. Results of recent tests by the U. S. navy are given. (Cf. Adamson, C. A. 17, 344.)

A. PAPINEAU-COUTURE

**The value of cryoscopy in the technical investigation of varnishes.** JOHANNES SCHIEBER AND OTTO NOUVEL. *Z. angew. Chem.* 36, 353-5(1923).—The detn. of av. mol. wts. by f. p. methods is useful in controlling the properties of bodied linseed oils and varnishes, suggests causes why certain resins produce inferior oil varnishes, etc. The mol. wts. of linseed oil detd. by using naphthalene as solvent in the f. p. method, agree with those of Seaton and Sawyer (C. A. 10, 1938): raw oil, 751 to 781; oil heated 6 hrs. at 200°, 702 to 784; 3 hrs. at 300°, 917 to 1168; 6 hrs. at 300°, 1128 to 1492. The mol. wts. of a large no. of "run" resins are tabulated. When linseed oil is added to these resins, the mol. wt. of the resultant varnish base is far higher than that calcd. from the mol. wts. of the individual constituents heated alone in the same manner. Exceptions are rosin-linseed oil and Borneo kauri-linseed oil bases in which the resultant mol. wts. agree with the calcd. wts. This indicates these resins simply form solns. while others form combinations with the oil, and explains why varnishes made with them are inferior to those made with other resins. The longer the period of heating, and the greater the proportion of oil to resin, the greater the difference between detd. and calcd. mol. wts. of the copal-oil mixts. The difference is greater in genuine kauri-linseed oil mixts. than in other resin-oil mixts.; this is in accord with the superior results obtained with kauri varnishes. Results are tabulated.

F. A. WERTZ

**Utilization of native [German] pines.** W. SCHULTZE. *Chem. Umschau* 30, 144-6, 151-3, 169-71(1923).—An account is given of the introduction by the German government of winning rosin from the native white pine forests during 1916-18. The overcoming of difficulties due to inexperience, improper tools and methods and the present state of this new industry are described.

P. ESCHER

Key industry of the South [naval stores] (HOLCOMBE) 23.

**Zinc white.** A. NITOUZ and C. CLERC. U. S. 1,463,483, July 31. Pptd. ZnCO<sub>3</sub> is redissolved in an acid soln. and ZnS is pptd. from this soln. by H<sub>2</sub>S to obtain a product which is relatively pure.

**Paints.** R. P. L. BRITTON AND GRIFFITHS BROS. & Co. (London), LTD. Brit. 191,426, Sept. 7, 1921. A paint is composed of a decorative base such as mineral pigments, and a liquid vehicle comprising an irreversible alk. silicic acid sol. The sol may be prepd. by grinding, in an alk. soln., silicic acid obtained by the action of acid on a sol. silicate; or by grinding and heating sand or SiO<sub>2</sub> with H<sub>2</sub>O, and grinding the product with a soln. of alkali. SiO<sub>2</sub> or diatomaceous earth may also be peptized by grinding in solns. of water-glass. The alkali content of the peptizing agent must be

sufficiently low to ensure that on drying the product shall be insol. in  $H_2O$ . Pigments not affected by the alkali present are preferably used.

**Varnishes.** WESTERN ELECTRIC CO., INC. Brit. 191,422, Sept. 5, 1921. Fatty acids are heated with either the gelatinized product formed by heating a vegetable oil with or without resin, or a mixt. of glycerol and resin with or without vegetable oil until the ingredients are thoroughly mixed and are on the point of gelatinizing. The compns., with or without diln. with solvents such as kerosene, are used as varnishes and are further heated after application to cause them to solidify. Suitable resins are shellac and Congo copal.

**Varnish.** R. S. LLOYD. U. S. 1,462,236, July 17. Crude pine sap is mixed with turpentine oil in the proportion of 1:3 and the mixt. is heated to about  $150^\circ$  to produce a varnish.

**Synthetic resins.** C. KULAS and K. PAULING. Brit. 191,417, Aug. 8, 1921. The elasticity of the resinous condensation products prepd. by the process described in 159,404, is increased by adding a mixt. of amyl alc. and glycerol, amyl alc. and camphor oil, or amyl alc., glycerol, and camphor oil, boiling off the  $H_2O$ , and hardening by heating at  $90$ – $100^\circ$  under atm. pressure. The products resemble amber, or, if a great excess of  $HCHO$  is used in the condensation, are ivory-like; in the latter case an addition of glacial  $HOAc$  after boiling off the  $H_2O$  is desirable.

**Turpentine substitute.** W. B. LOGAN. U. S. 1,463,122, July 24. A turpentine substitute is prepd. by subjecting pine oil vapors to the action of a  $Cu$  chloride catalyst at a temp. of  $225$ – $350^\circ$ , condensing the vapors, sepg.  $H_2O$  from them, fractionally distg. and collecting the fraction distg. up to  $200^\circ$ . The product has a sp. gr. of  $0.85$ – $0.86$ , contains about 90% of dipentenes and about 95% boils below  $190^\circ$ .

**Solutions of azo coloring substances in oil.** W. J. MURRAY. U. S. 1,462,613, July 24. An amine and a developer, e. g., dianisidine and  $\beta$ -naphthol, are dissolved in an oily substance such as oleic acid or an oil together with  $NaNO_2$  or other nitrite in order to form a soln. adapted for use in inks for prep. safety paper.

## 27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL.

**Promoters of the hydrogenation of oils.** I. SEICHI UENO. *J. Chem. Ind. Japan* 25, 777–83 (1922); cf. C. A. 13, 383; 15, 2201.—In the hydrogenation of herring and cottonseed oils with  $H$ ,  $Ni$  or  $Ni$  sulfate (0.3–0.5% as  $Ni$ ) being used as a catalyst, the presence of 2–3% of palmitic, oleic, stearic, or benzoic acid promotes the reaction. J. C. S.

**Composition of German bone grease.** K. FRICKE. *Z. deut. Oel-Fett-Ind.* 43, 401–2 (1923).—Recent deliveries of bone grease refused to crystallize after splitting and distg. Analytical investigation showed absence of fish and vegetable oils, the m. ps. of the sterol acetates ranging from  $114.5^\circ$  to  $115^\circ$ . There were present only 20–22% stearic, but 25–28% palmitic acid and the failure to crystallize is laid to this low % of stearic and high % of palmitic acid, probably due to disturbed conditions in the nutrition of the live stock. P. ESCHER

**Treatment by trichloroethylene (for fat extractions).** E. O. RASSER. *Chem. techn. ind.* 1922, No. 51, 1165–6; *Chimie et industrie* 9, 1190–1 (1923).—Brief discussion of the merits of  $C_2HCl_3$  for fat extrn. A. PAPINEAU-COUTURE

**Bleaching of beeswax, fats and oils.** CERA. *Seifensieder Ztg.* 50, 335–6, 347–8 (1923).—Detailed working directions are given for bleaching beeswax with  $K_2Cr_2O_7$ . The wax is first purified with dil.  $H_2SO_4$ , then bleached with 1%  $K_2Cr_2O_7$  and 2.6–2.8%  $H_2SO_4$  at a gentle heat, and finally washed free of any  $Cr$  with 1% oxalic acid. P. ESCHER

**The bleaching of oils and fats with benzoyl peroxide.** A. BOLIS. *Ind. saponiera* 23, 78–9 (1923).—A comparison of the  $K_2Cr_2O_7$  and benzoyl peroxide methods for bleaching vegetable oils and fats. The second is superior for edible oils in that it requires no subsequent removal of the oxidizing agent, leaves in the oil nothing but traces of  $PhCO_2H$  (which is innocuous), and is more economical. Furthermore, dark, inferior oil from olive-husks (which cannot be decolorized with  $K_2Cr_2O_7$ ) can always be bleached with 150–200 g. of benzoyl peroxide per 100 kg. of oil. Warning is given against the inferior com. grades of benzoyl peroxide, which may be very inactive. C. C. JAVIS

**Characteristics of Turkey red oils.** W. HERBIG and H. SEYFERTH. *Z. deut. Oel-Fett-Ind.* 43, 385–7 (1923).—By means of anhyd. acetone (for method see C. A. 8,

2809) two more Turkey red oils, Aviol KM and Monopol-brilliant-oil, were sepd. into a sol. and an insol. portion; these portions were examd. for their ability to "wet" yarn and for their  $n$ . The acetone-insol. Na salts showed an 8% greater "wetting" ability than the acetone-sol. and 12% greater than the original Aviol KM. They also showed a greater lathering ability. Under the ultramicroscope they were proved to consist of smaller particles than the sol. portion; the  $n_D^{25}$  of the original Aviol KM was 1.4056 and that of the acetone-sol. portion 1.4772. The following improved method for *deig.*  $SO_2$  present as  $Na_2SO_4$  is given: To 10 g. in a separatory funnel add 10 cc. ether and 5 cc. benzene and shake out 3 times each with 20 cc. satd. NaCl soln; in the united exts. det. the  $SO_2$  as  $BaSO_4$ ; the NaCl exts. will clarify after standing 15-30 min. The results agree closely with control detns. Further work on the character of the portions sepd. by acetone is in progress.

P. FISCHER

The occurrence of nitrogenous material in fats and oils and its determination. E. UTZ. *Chem. Umschau* 30, 161-5 (1923).—From a review of the literature and from his own investigation U. concludes that the statements in textbooks (Benedict-Ulzer) about the occurrence of 1.0-1.5% protein in oils and fats are incorrect; the actual amts. found by U. were 0.05-0.17% protein.

P. FISCHER

Composition of the fatty acids of rape oil. YOSHIYUKI TOYAMA. *J. Chem. Ind. Japan* 25, 1044-53 (1922); cf. *J. Tokyo Chem. Soc.* 16, 187 (1895).—The main constituent of the fatty acids of rape oil obtained from the seeds of *Brassica campestris*, L. (*B. chinensis*, L.), grown in the Shiga prefecture, was erucic acid (about 65%). The satd. acids (less than 2%) consisted of palmitic acid with seemingly stearic; behenic, lignoceric, and arachidic acids. The presence of linolenic, linolic, and oleic acids was proved from the bromination and oxidation of the liquid acids and their Me esters.

J. C. S.

Seeds of *Prunus brigantia* Vill. and their oil. L. KAVAJOLI. *Boll. assoc. ital. piante med. arom. util.* 4, 38-41 (1921); *Bull. Agr. Intelligence* 12, 564-5 (1921).—One hundred g. of the fruit of this shrub yield approx. 69 g. of stones which consist of 32% kernel and 68% shell. The shells contain 0.42% ash. The kernels have the following gross compn.: 7.60%  $H_2O$ , 2.44% ash, 23.12% crude protein, 48.01% crude fat, 3.51% crude fiber, and 15.32% N-free ext.; their ash is rich in  $P_2O_5$  (35.57%) and K, and contains Ca, Mg and sulfate as well as small amts. of Fe and Cl; they contain 16% free lecithin, 0.21% combined lecithin, 0.123% total HCN, 0.048% preformed HCN, 1.25% amygdalin, 4.3% reducing sugar calcd. as glucose, and a small amt. of starch. On pressure, the kernels yield as much as 35 or 40% of their wt. as *marmole oil* which is light yellow and slightly bitter, has a marked odor of bitter almonds, and is consumed either pure or mixed with olive oil. The oil has the following consts.: sp. gr. at 15° 0.9178, refractive index (oleorefractometer) 64.5°, f. p. 19°, saponification no. 194.9, acid no. 4.6, ester no. 190.3, I no. 89.4, acetyl saponification no. 218.8, volatile fatty acids trace; fatty acids f. p. 7°, m. p. 10°, refractive index 51°, and, after acetylation, 53°. The press cake is used as a cattle food, but only in limited amts. on account of its HCN content.

JOSEPH S. HEPBURN

Some fish oils of the Madras Presidency. A. K. MENON. *Proc. 7th Indian Sci. Cong.* 1921, lxxvii-viii.—The chief oil is sardine oil (*Clupea longiceps*). It is obtained by boiling the fish, skimming the oil and pressing the residue; the yield is 10% by wt. It is used for leather, jute, tempering steel, calking boats, because of a high % of unsatd. fatty acids for paint and varnish, and the golden pale skimmed oil in wasting diseases. When hydrogenated it is odorless with the appearance of stearin and can be used for candles and an insecticidal soap. The guano (the residue after removal of oil) is a good fertilizer. Fish oil is obtained also from the livers of sharks, skates, etc.

C. C. DAVIS

A highly unsaturated hydrocarbon, and some higher alcohols in a commercial illipé fat. SHŌMEI KOBAYASHI. *J. Chem. Ind. Japan* 25, 1188-96 (1922).—A new, highly unsatd. hydrocarbon, *illipene*,  $C_{22}H_{36}$ , a light yellow solid with an aromatic odor, m. 64.5°, I value 382.5, was isolated from the unsaponifiable matter (8.55% of the fat) of a com. illipé fat imported from India. It is optically inactive and  $b_D^{25}$  315°. The *hydrochloride* is a white powder, m. 115-16°. The unsaponifiable matter also contains 4 higher alcs. which were sepd. by repeated recrystn. from acetone: (I)  $C_{24}H_{48}O$ , microscopic, silky needles, m. 196-7°, I value, 114.9°; (II)  $C_{26}H_{52}O$ , silver-white crystals, m. 186-186.5°, I value, 100.2; (III)  $C_{27}H_{54}O$ , silver-white grains, m. 159-60°, I value 82.3; and (IV)  $C_{27}H_{56}O$ , light yellow needles, m. 125-35°, I value 100.2. The solid mixt. of fatty acids of the fat is mainly composed of stearic acid.

J. C. S.

Studies on the hydrolysis of fats and oils. III. Twitcheil's reagent and its application. I. GEN-ITSU KITA AND TSUNETARO YAMANO. *Bull. Inst. Phys. Chem. Research (Japan)* 2, 169-188 (1923).—For the prepn. of the reagent a mixt. of PhOH and fatty acid from rape-seed oil is mixed with  $H_2SO_4$  at low temp. and allowed to react for

5-24 hrs.; longer reaction decreases the yield and activity of the product. The time and temp. of the washing with water have a slight effect on the yield and the  $H_2O$  content of the product. The optimum quantity of  $H_2SO_4$  is 75 cc. for a mixt. of 50 g. of fatty acid and 17 g. of  $PhOH$ . The proportion of fatty acid for a definite amt. of  $H_2SO_4$  and  $PhOH$  has a large effect on the yield but almost no effect on the activity of the product. Fatty acids obtained from hardened soy-bean, castor, soy-bean, linseed, and herring oils gave less reactive reagent than those from fatty acids of rape-seed and olive oils. Of  $PhOH$ ,  $C_6H_6$ , naphthalene, and anthracene, naphthalene gave the most active reagent, while anthracene gave the weakest one; those from  $PhOH$  and  $C_6H_6$  resemble that from naphthalene.  $H_2SO_4$  (0.05-0.1% of the fat to be decomposed) accelerates the action of the reagent, but the action is not proportional to the amt. of the acid. By purification the activity of the reagent is increased, but the unpurified reagent is better for practical purposes. Small amts. of salts, insol.  $PbSO_4$ , and wood of the reaction vessel have almost no effect on the reactivity of the reagent, but large amounts of salts, *e. g.*,  $Na_2SO_4$ ,  $CuSO_4$  or  $MgSO_4$ , have a bad effect. The activity of the reagent is destroyed by washing with  $NaCl$  soln. Of herring, whale, coconut, and soy-bean oils and beef tallow, the decompn. of soy-bean oil is most difficult. In industrial expts., 1,000 kg. of beef tallow were decomposed with 1% of the reagent, prepd. from 0.045 kg. of fatty acid of rape-seed oil, 4.343 kg. of naphthalene and 21.124 kg. of  $H_2SO_4$  of 65° B $\acute{e}$ , and 1% of the same  $H_2SO_4$  in a wooden vessel (capacity 3 tons and lined with  $Pb$  plate), under a current of steam; the  $H_2O$  content was so regulated as to be 50% after decompn. 90.9% of the fat was decomposed after 15 hrs.; then glycerol- $H_2O$  was sepd. and treated with 0.25% of the reagent and the same amount of  $H_2SO_4$  of 65° B $\acute{e}$ . for 6 hrs.; a total of 98.5% of the fat was decomposed. K. K.

**Progress in the soap industry.** J. LEIMDÖRFER. *Chem. Umschau* 30, 149-51, 157-61 (1923).—A discussion of M. H. Fischer's expositions of the similarity in behavior of soaps and albumins through the co-existence of 2 systems, *viz.*,  $H_2O$  in soap and soap in  $H_2O$ , and L.'s views on the relation of org. matter to organized life. An abstract is given of a Ger. patent by the "Vereinigte Chem. Werke, Charlottenburg," according to which neutral oils are saponified with  $Na_2CO_3$  in open kettles at 140-200°, with 13-50%  $H_2O$  on the fat basis (13% when a reflux condenser is used); the resulting concd. soap is salted out and the kettle contents are finally dild. to the normal amt. of  $H_2O$ . *Milled soaps* can now be made directly by passing kettle soap over hot drying rolls which evap. its  $H_2O$  down to 82% fatty acid content in less than 1 min., and pressing the resulting powdered but plastic soap into cakes by means of hydraulic presses. This process is also applicable to laundry-soaps with a high % of fatty acids, making the use of hardened fats superfluous, because many oils will yield a soap of proper consistence when thus concd. The permanence of soap lather is due to the emulsoid character of the soap soln; a new colloidal system is formed in the latter, one constituent being a gas ( $O$  when compds. are present that liberate  $O_2$ ), the other a liquid; in order to obtain permanency of a lather, the emulsoid must possess viscosity, which may be obtained either by increasing the soap concn., by adding glycerol or by converting the emulsoid into an emulsion by means of an excess of fat. P. ESCHER

**Bile and bile soaps.** F. H. ZSCHACKE. *Z. deut. Oel-Fett-Ind.* 43, 321-3, 339-41 (1923).—Expts. are detailed in which dild. bile and undild. bile were tested for lathering power, emulsification of oils and dispersion of clay, alone and in combination with soaps, in distd. and in hard  $H_2O$ , boiled and unboiled, in neutral and in alk. solns. Soaps contg. such small amts. of bile as are found in com. bile soaps possess no greater lathering or cleansing power than ordinary soaps; it requires greater additions of bile than are practical to produce a notable increase in lathering. Bile alone, without soap, produces some lather but its coloring matter has a tendency to deposit on the washed goods. P. ESCHER

**Solid fats.** ANON. *Seifensieder-Zig.* 50, 281-2, 296 (1923).—A popular article on the properties, uses and methods of splitting glycerides of fatty acids. P. ESCHER

**Solid potassium soaps.** TH. LEGRADI. *Z. deut. Oel-Fett-Ind.* 43, 369-70 (1923).—A brief recapitulation of the production and properties of solid K soaps. P. ESCHER

**Purification of castor oil.** HARUBUMI KUME. *Japan.* 41,338, Dec. 27, 1921. Addp. to 40,191 (C. A. 17, 1348). By heating at 100° for 40-50 min. in a closed vessel under agitation a mixt. of crude castor oil (100 parts) and astringent juice (25 parts) prepd. from persimons, proteins and viscous material in the oil is coagulated by tannic acid in the juice. The oil is sepd. from the ppt., mixed with the same amt. of  $AcOH$ , sprayed into a chamber contg. superheated steam, filtered, heated with 4-5% satd. bleaching powder soln. at 100°, neutralized with  $Ca(OH)_2$ , washed with  $H_2O$ , heated with 6-8%



Japanese acid clay and filtered. The oil is then heated with a dil. mixt. of  $\text{NH}_3$  and  $\text{Na}_2\text{CO}_3$  at  $100^\circ$ , washed with  $\text{H}_2\text{O}$ , boiled with 10% Japanese acid clay, filtered, and blown with hot air for 3-5 hrs.

**Soap.** P. L. F. PACH. U. S. 1,462,243, July 17. A soap which is adapted for use with sea water is prepd. from coconut oil 100,  $\text{NaOH}$  4.75, Na silicate 5,  $\text{KOH}$  6 and a 1%  $\text{KClO}_3$  soln. 100 parts.

**Apparatus for extraction of beeswax from slumgum.** E. H. CUMMINS. U. S. 1,463,154, July 31.

## 28 - SUGAR, STARCH AND GUMS

F. W. ZERBAN

**Report (No. 78) on the most important articles in the 2nd half of 1922 in the field of the pure chemistry of sugars.** EDMUND O. VON LIPPIMANN. *Deut. Zuckerind.* 48, 57, 60, 83-4, 97, 109-10(1923). W. L. BADGER

**Final report on the mill control in 1922 (Java).** *Arch. Suikerind.* 31, Mededeel. Proefstation Suikerind. No. 6, 243-89(1923). F. W. Z.

**System of mill control for 1923.** ANON. *Arch. Suikerind.* 31, 560-76(1923).—Blank forms for the semi-monthly reports of the mutual factory control in Java. F. W. ZERBAN

**System of fuel control for 1923.** ANON. *Arch. Suikerind.* 31, 577-83(1923); cf. preceding abstract.—Similar blank forms for fuel control. F. W. Z.

**Machinery for the extraction of cane sugar.** F. MERTZ. *Z. Ver. deut. Ing.* 67, 453-5(1923).—Description of a Krupp 11 roll mill. W. L. BADGER

**Sugar machinery.** LORD INVERNAIN. *Engineering* 115, 817-20(1923).—The development of machinery used in the cane sugar industry is traced from the yr. 1800, and its effect on the quantity and quality of the sugar produced is shown. The importance of chemical control is pointed out. One effect of the improvement in milling machinery is the large amt. of finely divided fiber in the juice from modern mills, which is not removed by present methods of clarification. Special mention is made of the *Mauou centrifugal separator* as a means of overcoming this difficulty. It removes suspended matter from raw juice continuously and automatically, facilitating all subsequent operations, particularly clarification, and improving the quality of the sugar. Illustrated. F. W. ZERBAN

**Continuous diffusion.** J. KNOBLOCH. *Centr. Zuckerind.* 31, 401-3; *Deut. Zuckerind.* 48, 84-6(1923).—A description of Raabe's "Rapid" continuous extn. device. It consists of a slightly inclined stationary cylinder, with cross partitions dividing it into 23 sections. These partitions occupy a little more than the lower half of the cross-section of the cylinder, have a perforation near the top and a metal screen a little distance from the partition on the upper side. A central horizontal shaft (3 r. p. m.) has stirring arms for each section. The cylinder is enlarged over the bottom 7 sections. Chips are heated to  $85^\circ$  by exhaust steam in the slicer and charged into the lower end. Fresh water warmed to  $40^\circ$  is fed into the upper end. The chips are passed up through the cylinder, and lifted over the partitions by the stirring arms. The juice passes down, rising to the perforation in the top of the partitions behind the screens. In the 7th section from the top, pulp press water is added. Raw juice is withdrawn from the lowest section. In the campaigns of 1921-22 (a) and 1922-23 (b) results were: press juice, Brix (a) 19.08, (b) 19.50; purity (a) 89.1, (b) 86.7. Raw juice, Brix (a) 15.5, (b) 14.9; purity (a) 89.6, (b) 87.7. Sugar in pressed pulp, (a) 0.73, (b) 0.81; pulp in % on beets both (a) and (b) 67.0. Draft was 110%. Heat balances for 100 kg. beets show 9793 Cal. used in this app. and 10,055 in a diffusion battery. Power consumed was 12-15 h. p. (Cf. Szavsky, C. A. 17, 2200.) W. L. BADGER

**Device for the automatic separation of (green) sirup (from wash sirups).** FRANZ SCHIFFER. *Z. Zuckerind. czechoslovak. Rep.* 47, 357-60(1923).—Under the discharge pipe for green sirup is a trough, mounted on trunnions and large enough to hold the green from one filling of the centrifugal. It is held in place by a counterweight and levers. The counterweight is set for the amt. of green expected. When this is reached the levers shift automatically and the measuring trough dumps into a launder. It locks in this position, but in this position it holds a funnel under the discharge pipe, so that the wash sirup is directed into another launder. A system of levers connected with the valve for massecuite restores the trough to the position for receiving green when a new charge is drawn. W. L. BADGER

**The use of the refractometer in the individual examination of sugar beets.** O.

MUNERATI AND G. MEZZADROLI. *Stas. sper. agrar. ital.* **55**, 163-72(1922).—The refractometer (sugar type) should be considered a very useful instrument in the individual analysis of beets. It cannot, however, replace the polarimeter except where an approx. idea of the sugar content suffices. The data obtained with the polarimeter and refractometer supplement and control each other. Refractometric examn. can replace, because of greater exactness and convenience, the method of immersion of the beets in salt or sugar solns. of definite densities for classification according to their sp. gr. (as detd. by their floating or sinking). A 2nd polarimetric examn. (ordinarily carried out in selection labs. as a control on individual beets indicated as having a high sugar content in the 1st analysis) can be replaced by a refractometric examn. which is equally accurate and avoids the possible injury to the beet involved in 2 immersions. The simple refractometer can render very useful service in those cases where it is sufficient to ascertain the d. (dry matter) of the juice only and where a rough estimate of the value of a beet is desired without polarimetric examn.

ALBERT R. MERZ

The thiocyanate-potassium iodide method and Herzfeld's invert sugar table. G. BRUHNS. *Z. Zuckerind. czechoslovak. Rep.* **47**, 373-8(1923).—After reducing 50 cc. Fehling soln. with a 50 cc. sample in the usual way, add at once 100 cc. cold  $H_2O$ , cool rapidly, pour off into a 250-cc. graduated flask, rinse over any  $Cu_2O$  with a little cold  $H_2O$ , and make up to vol. To 100 cc., add 5 cc. of a soln. contg. 65 g. KCNS and 10 g. KI in 500 cc., add also 10 cc. 6-6.5  $N$   $H_2SO_4$ . Titrate to the usual I end point with starch indicator, with 0.1387  $N$   $Na_2S_2O_3$  soln. made alk. with 2-3 cc.  $N$  NaOH. Also make a blank titration on the original amt. of Fehling soln. The difference is  $Cu$  pptd. as  $Cu_2O$ . This method gives accurate results with Herzfeld's, Baumann's or Bruhn's tables for invert.

W. L. BADGER

The gasometric determination of carbon dioxide in materials in the manufacture of sugar. H. SPIELHACZEK. *Z. Zuckerind. czechoslovak. Rep.* **46**, 459-61; *Chem. Zentr.* **1922**, IV, 677.—The app. devised by Donath and Ehrenhofer for gasometric detn. of C in Fe and steel (*Monat. Rundscha* **45**, 285) is recommended as useful in the detn. of smaller amts. of  $CO_2$ . The manipulation of the app. (obtainable from Franz Hugershoff, Leipzig; A. Eberhard, Berlin) is explained and illustrated. The app. serves for the detn. of  $CO_2$  in defecation slime, limestone, satn. gases, etc.

C. C. DAVIS

The manufacture of corn sugar. J. K. DALE. *Chem. Age (N. Y.)* **31**, 295-6(1923).—Descriptive.

E. H.

A method for the rapid titration of dark solutions (KRYZ) 7. The sources of the rare sugars (HARDING) 10.

## 29—LEATHER AND GLUE

ALLEN ROGERS

The system tannin: non-tans plus hide substance: nitrogenous matter other than hide substances. W. MOELLER. *Z. Leder- Gerberei Chem.* **2**, 15-20(1922).—M. criticizes quant. and qual. methods of distinguishing tans from non-tans, and states that the properties of the different vegetable tannins are a function of the properties of the peptizer present in the tanning material. Until recently the hide was considered to be transformed into a single substance, "pelt," which was the raw material for leather manuf. Pelt is not a single substance, but consists partly of material which will form leather and partly of material which will not. Some part of the hide can be removed by water and part of the leather also is sol. in hot water. There is no method of detg. the ratio "hide substance": "not-hide substance" in pelt, which is progressively affected by certain tanning materials. The hot-water test on finished leather gives some information.

J. C. S. I.

Hydrolytic action of some clarifying, decolorizing and solubilizing agents for vegetable tannin extracts on hide substance. W. MOELLER. *Z. Leder- Gerberei Chem.* **2**, 1-15(1922).—Mineral decolorizing and solubilizing agents, such as Al sulfite and bisulfite, in the pure state, have an appreciable hydrolytic action on hide substance independent of the concn. but proportional to the time of action. Certain org. sulfonic acids and carboxylic acids are quite indifferent to hide substance, and their use is advantageous to the tanning industry. Such substances peptize or dissolve the difficultly sol. tannin phlobaphenes.

J. S. C. I.

The adsorption of chrome from chrome liquors by hide substance and negative adsorption. A. W. THOMAS. *J. Am. Leather Chem. Assoc.* **18**, 423-30(1923).—The adsorption of Cr by hide substance cannot be measured by the drop in concn. of chrome

liquor upon shaking with hide powder. Conc'd. chrome liquors are rendered even more conc'd. through contact with hide powder, even though some Cr is removed from soln. by combining with the hide substance, because the hide jelly absorbs a soln. much more dil. than the remaining unabsorbed soln. The results constitute a fulfilment of the prediction made by Williams (*C. A.* 8, 2093) regarding negative adsorption. Schultz's criticism of the work of Thomas and Kelly (*C. A.* 15, 610) on the ground that their findings were the result of pouring chrome liquors on to dry hide powder was shown to be without foundation by a repetition of the work, with hide powder soaked in water for 15 hrs. before addition of the chrome liquor. The results show an apparent verification of the prediction made by Wilson and Gallun (*C. A.* 14, 2728) that the curve representing the fixation of Cr by hide substance as a function of concn. should have a point of min. at some high concn., beyond which there is increasing fixation.

J. A. WILSON

**Degree of dispersion as an influence in tanning.** JEROME ALEXANDER. *J. Am. Leather Chem. Assoc.* 18, 400-9(1923).—An elementary exposition of some popular views of colloid chemistry. The speculation is made that possibly the several tanning exts. owe their differences in tanning action to substances exerting a protective action upon the tannin to different degrees and bringing about differences in degree of dispersion of the tannin.

J. A. WILSON

**Action of acids on hide.** G. GRASSER. *Z. Leder- Gerberei Chem.* 2, 113(1922); *J. Am. Leather Chem. Assoc.* 18, 452-3(1923).—At the same normality, different acids show very different degrees of action upon hide. Hydrolytic and swelling effects are described.

J. A. WILSON

**Remarks on chrome tanning.** G. GRASSER. *Z. Leder- Gerberei Chem.* 2, 110(1922); *J. Am. Leather Chem. Assoc.* 18, 454(1923).—A discussion of the manuf. of Cr liquors and of the neutralization of Cr leather.

J. A. WILSON

**Turkey red oil.** G. GRASSER. *Z. Leder- Gerberei Chem.* 2, 112(1922); *J. Am. Leather Chem. Assoc.* 18, 454(1923).—A recommendation to use sulfonated castor oil for fat-liquoring and finishing leather.

J. A. WILSON

**Importance of swelling for sole-leather manufacture.** G. GRASSER. *Z. Leder- Gerberei Chem.* 2, 113(1922); *J. Am. Leather Chem. Assoc.* 18, 453-4(1923).—It is important to regulate the acid concn. as well as the tannin content of liquors used to tan sole leather.

J. A. WILSON

**Grain defects and their cause.** G. GRASSER. *Z. Leder- Gerberei Chem.* 2, 115(1922); *J. Am. Leather Chem. Assoc.* 18, 454(1923).—Defects appearing on the grain side of leather are often due to improper treatment of the raw skin, such as failure to guard against bacterial action or the presence of injurious materials in the salt used in curing.

J. A. WILSON

**The ultra-filtration of tannin and other solutions.** R. J. BROWNE. *J. Am. Leather Chem. Assoc.* 18, 409-23(1923).—An ultra-filter is described designed to sep. tannin from nontannin. On the assumption that all of the nontannin passed through the filter, under the conditions of the tests, it was found that its quantity agreed closely with that obtained by applying the official method of tannin analysis of the Society of Leather Trades' Chemists to the tanning ext. exam'd. Pyrogallol, resorcinol, and gallic acid passed through the ultra-filter quant. Catechol did not pass through completely, but the portion retained by the filter had acquired the property of pptg. gelatin solus. The prepn. of membranes of different permeability is described.

J. A. WILSON

**The elucidation of the details of the method for the determination of free sulfuric acid in vegetable-tanned leather, committee report, 1922-23.** J. S. ROGERS, *et al.* *J. Am. Leather Chem. Assoc.* 18, 430-8(1923).—The Procter-Searle method is recommended provisionally. The effects of the presence of substances likely to interfere with the detn. are discussed.

J. A. WILSON

**The color measurement of vegetable tannin solutions, committee report, 1922-23.** T. BLACKADDER, *et al.* *J. Am. Leather Chem. Assoc.* 18, 438-40(1923); *cf. C. A.* 17, 2201.—A table is given showing the extent to which it was possible for 4 labs. to obtain concordant results. When tanning exts. were dissolved in hot water and cooled rapidly to make the measurements, the solns. were of a lighter color than when the cooling was allowed to proceed slowly.

J. A. WILSON

**Determination of tannin.** G. GRASSER. *Z. Leder- Gerberei Chem.* 2, 20-6(1922).—The official shake method gives very unreliable results. Analyses of the same material by different labs. lead to widely varying results, *e. g.*, 25.4%-29.1% tans in a liquid chestnut ext., whereas the filter-ball method gives better concordance, *e. g.*, 31.6% to 32.1% tans. The results given by the shake method do not correspond with the practical value of the materials. A second detannization of the tanning sola. in the

shake method of analysis removes a further portion of "tans" and the "non-tans" are then colorless.

J. S. C. I.

**Determination of chrome in chrome leather, committee report, 1922-23.** L. BALDERSTON, *et al.* *J. Am. Leather Chem. Assoc.* 18, 441-4 (1923).—After the leather ash has been fused with  $\text{Na}_2\text{CO}_3$ , it should be extd. with water and filtered free from iron before acidifying; the presence of iron salts in the soln. to be titrated causes high results.

J. A. WILSON

**Treating hides.** SRES NOREDNLYCHT. *Brit.* 191,431, Sept. 13, 1921. A compn. for use in unhairing hides, skins, etc., consists of an alkali bisulfide and free alkali, the latter being insufficient in quantity to convert the bisulfide into the monosulfide. The compn. is prepd. by the decompn. of an alk. polysulfide with caustic alkali. The S in a finely divided state is dissolved in a strong soln. of the alkali heated to about 80°, and the further amt. of alkali, which is preferably in slight excess of the amt. required to convert all the pentasulfide into the bisulfide, is then added.

**Tanning leather for shoe uppers.** D. G. CARTER. U. S. 1,463,066, July 24. Seamless uppers are prepd. from green hide shaped to a last by tanning while so shaped for a sufficiently long period to set the leather in shape. Similar-shaped tanned pieces are nested together after removal from their lasts and the nested uppers are subjected to a further tanning treatment.

**Imitation leather.** ETSUJI ASHIDA. *Japan.* 41,617, Jan. 31, 1922. An intimate mixt. of elastic rubber 600, hydrated cellulose 650, glue 120, S 40,  $\text{Mg}(\text{OH})_2$  250,  $\text{ZnO}$  100, lactice 30, paraffin 15, and  $\text{Sb}_2\text{S}_3$  35 parts is compressed into a mold and vulcanized for 1-1.5 hrs. under 40-60 lbs. steam. The product is soft and flexible and strong.

### 30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

**Recent important investigations in the chemistry of rubber, and substantiation of the  $\text{C}_2\text{H}_2$  ratio.** H. L. FISHER. *Ind. Eng. Chem.* 15, 860-2 (1923).—A review.

C. C. DAVIS

**Rubber from sprayed latex.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 224-5 (1923).—A further sample of sprayed rubber (cf. *C. A.* 17, 1349) examd. in a pure gum mixt. cured 30% faster than av. smoked sheet samples but no faster than sheet prepd. by  $\text{AcOH}$  coagulation from  $\text{NH}_3$ -preserved latex; its tensile strength, however, was somewhat better than that of the latter sheet. Analytical figures for the samples are given. A comparison of the properties of sprayed rubber with those that have been recorded for rubber prepd. by the evapn. of latex by the Kerbosh process indicates a general similarity in the properties of these two forms.

G. S. WHITBY

**Rubber coagulated with fluosilicic acid and its salts.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 382-3 (1923).—Samples previously examd. in a rubber-S mixt. (*C. A.* 17, 2203) were further examd. in the mixt. rubber 90:S 10:PbO 50. In this mixt.  $\text{H}_2\text{SiF}_6$  has no retarding effect on the rate of cure. Pb, Zn, and Mg fluosilicates give similar results; and these results are similar to those which  $\text{Na}_2\text{SiF}_6$  gives. Na,  $\text{NH}_4$ , and K bifluorides give similar results, except that the rubber coagulated with the first cured rather more slowly than the rubber coagulated with the other agents. All the substances mentioned appear to be satisfactory coagulants.

G. S. WHITBY

**Bulk tests with sodium fluosilicate.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 296-8 (1923).—Coagulation with  $\text{Na}_2\text{SiF}_6$  was found to have a very marked mold-preventing effect on two lots of sheet the cases contg. which were in one instance exposed to rain and in the other dropped into water. As found before, sheet prepd. by  $\text{Na}_2\text{SiF}_6$  cured in a rubber-S mixt. more slowly than sheet prepd. by  $\text{AcOH}$ .

G. S. W.

**Effect of soaking sheet in sodium fluosilicate solution.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 383-4 (1923).—Slaking sheet for 1 hr. in a soln. of  $\text{Na}_2\text{SiF}_6$  (0.66%) with the object of preventing the growth of mold reduces the rate of cure in a rubber-S mixt.

G. S. W.

**Notes on the "creaming" or separation of preserved rubber latex.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 216-7 (1923).—There seps. on standing from some samples of latex preserved with  $\text{NH}_3$  a "cream," which, when removed and shaken up with water, forms an emulsion that has all the properties of uncoagulated latex and in which microscopic examn. reveals only discrete particles. Attempts to obtain such

a cream by centrifugating preserved latex, however, met with no success. In an ordinary milk separator semi-coagulated rubber collected on the baffle plates. (Such sepn. took place more readily from latex preserved with NaOH + a coal-tar product than from latex preserved with  $\text{NH}_3$ .) In an ordinary type of centrifuge no sepn. occurred. In a centrifuge consisting of a rotating bowl running at speeds up to 40,000 r. p. m. a thick cream sepd., but could not be handled, as the slightest pressure caused the globules to adhere and form a clot. The reason for this last-mentioned state of affairs is probably that the speed required to sepn. the globules from *Hevea* latex is so high that the sepd. globules become compacted. G. S. WHITBY

**Vulcanizing properties of rubber from preserved latex.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 225-6(1923); cf. *C. A.* 17, 2203.—The rates of cure of (a) a sample of rubber coagulated from latex preserved with ammonia, (b) 3 samples coagulated from latex preserved with NaOH + a coal-tar product, (c) 2 samples of sprayed rubber were compared in a 90:10:7 rubber-S-PbO mixt. The sample (a) cured fastest and the samples (c) most slowly. G. S. W.

**Effect of resting on the rate of cure.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 381-2(1923).—Three samples of rubber prepd. immediately after trees had rested for 4 mos. were compared with a sample prepd., later, after the trees had been in tapping for 2 mos. Contrary to the results of de Vries, the former were found to cure more slowly than the latter. (Cf. *C. A.* 16, 4363.) G. S. W.

**Organic accelerators and plantation rubber.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 202-6(1923).—Seven samples of rubber representing markedly different types were compared, as regards rate of cure, in a rubber-S mixt. and in mixts. contg. ZnO and (a) thiocarbamide, (b) hexamethylenetetramine. The samples showed wide variation in the pure gum mixt.; less in the presence of (a); and less still in the presence of (b). The accelerators did not, however, by any means eliminate variation. The order in which the samples fell in the presence of the accelerators was not dissimilar to that in which they fell in their absence. Preliminary tests in which the proportions of (a), of (b) and of S were varied are recorded. G. S. WHITBY

**Rubber-formolite.** F. KIRCHHOFF. *Chem.-Ztg.* 47, 513(1923).—In continuation of research on the  $\text{H}_2\text{SO}_4$ -transformation products of rubber (cf. *C. A.* 15, 960; 16, 1885) the reaction of these compds. with  $\text{HCHO}$  was studied. Pale crepe dispersed in petr. ether was shaken with concd.  $\text{H}_2\text{SO}_4$  and let stand until yellow amorphous flakes appeared. It was then shaken with  $\text{HCHO}$  until a greenish brown, flocculent ppt. was formed, which on standing at  $100^\circ$  became brownish. When cool, the supernatant liquor was removed, the ppt. washed with hot  $\text{H}_2\text{O}$ , ground fine, treated with concd.  $\text{NH}_4\text{OH}$  (changing the color to golden brown), again ground, extd. with  $\text{H}_2\text{O}$  until no  $\text{SO}_4$  could be detected, and dried at  $95^\circ$ , giving a yield of approx. 2 g. of pure rubber-formolite per g. rubber. Rubber-formolite is a bright ochre-yellow, velvety powder, decomps. when heated without fusing, insol. in solvents of the  $\text{H}_2\text{O}$  type, but swells in  $\text{CS}_2$  and  $\text{C}_6\text{H}_6\text{N}$  (brown-red color). Treated in  $\text{CCl}_4$  with Br and let stand, a dark brown powder sepd., which, washed with  $\text{Me}_2\text{CO}$  and dried at  $80^\circ$ , showed a Br absorption of 12.6% (corresponding to  $\text{C}_{20}\text{H}_{20}\text{Br}$  based on the original rubber). Since the rubber- $\text{H}_2\text{SO}_4$  product adds 37% Br (corresponding to  $\text{C}_{20}\text{H}_{20}\text{Br}$ ), the formolite compd. was probably formed by an addn. or a rearrangement at the location of a former double bond. C. C. DAVIS

**Effect of mold on a sheet rubber compounded with litharge.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 341-2(1923).—Although a sample of sheet rubber which had become moldy as a result of a night's exposure to rain behaved normally in a pure gum mixt., it cured with exceptional slowness in a mixt. contg.  $\text{PbO}$ . G. S. W.

The measurement of temperature in rubber and insulating materials (SPEAR, PURDY) 2.

**Filler for rubber.** A. W. GOULD. U. S. 1,463,781, July 31. Powdered calcined tufaceous breccia is used as a filler in rubber compns.

**Lubricating rubber molds.** A. G. VOITZ. U. S. 1,462,563, July 24. Molds for molding rubber are sprayed with a compn. prepd. by boiling stearin in  $\text{H}_2\text{O}$  and adding Na borate,  $\text{NH}_4\text{OH}$  and NaCl.

